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Dual effects of sodium sulfide on the flotation behavior of chalcopyrite: I. Effect of pulp potential

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Abstract: This study explores the flotation behavior of chalcopyrite in the presence of different concentrations of sodium sulfide ($Na_2S{\cdot}9H_2O$) at pH 12 under controlled potential conditions. It was observed that the flotation of chalcopyrite is not depressed completely when the pulp potential is low, even at high concentrations of sodium sulfide, i.e., 10^{-1}–10^{-2} mol/L. However, a partial and controlled oxidation of pulp does enhance the effectiveness of sodium sulfide on the depression of chalcopyrite. Characterization of the chalcopyrite particle surface by X-ray photoelectron spectroscopy allowed the identification of hydrophilic and hydrophobic surface species, which are responsible for the depression and flotation of chalcopyrite. Changes in pulp potential were found to be an effective float controlling parameter, by which Na_2S can be used to initiate or depress the flotation behavior of chalcopyrite.

Keywords: chalcopyrite; flotation; electric potential; sodium sulfide

1. Introduction

Sodium sulfide ($Na_2S{\cdot}9H_2O$) has been widely used as a reagent in flotation processes [1–2]. Literature sources have discussed the applicability of sodium sulfide as a sulphidizing agent in the flotation of oxide or silicate minerals [3–4], as an activator in the flotation of sulfide minerals [5–6], particularly in the collectorless flotation of chalcopyrite [7–9], and also as a depressant of copper and iron bearing sulfide minerals such as the flotation separation of molybdenite from bulk copper-molybdenum concentrates [1,10–11]. In the Sarcheshmeh Copper Complex, located in the Kerman Province, southeast of Iran, sodium sulfide is also used as the copper and iron bearing mineral depressant in the molybdenite enrichment plant. Sometimes, copper and iron grades increase in the molybdenite concentrate despite the great care and the high consumption of sodium sulfide. Mineralogical observation has shown that chalcopyrite is the primary copper sulfide within molybdenite concentrates. The generally accepted depression mechanism of sulfide minerals in the presence of sodium sulfide is the collector removing effect of Na_2S which proceeds as follows [1,10–11]:

$$2CuX + HS^- + OH^- \rightarrow Cu_2S + H_2O + 2X^- \quad (X = \text{Xanthate}) \tag{1}$$

The hydrosulfide ion (HS^-) which is the result of hydrolysis and dissociation of sodium sulfide, removes the collectors from the chalcopyrite surfaces and makes it unfloatable. Another factor responsible for the flotation of chalcopyrite in the presence of high concentrations of sodium sulfide is discussed in this study. A preliminary investigation measured the oxidation–reduction potentials of different parts of the circuit. The results revealed large changes in pulp potential during flotation and regrinding processes in the Sarcheshmeh molybdenite enrichment plant. It is suggested that pulp potential can affect the depressant role of sodium sulfide. It is known that pulp potential and the oxida-

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tion–reduction state of pulp have significant influence on the flotation of sulfide minerals [12–22]. Although several studies have investigated the depression and activation effects of sodium sulfide on the flotation of sulfide minerals [1,5,7–10], there is no significant information regarding the relationship between the dual effects (initiation and depression) of sodium sulfide and pulp potential variations. This study investigates the influence of pulp potential on the dual effect of sodium sulfide on the flotation behavior of chalcopyrite. To identify the surface species responsible for the flotation and depression of chalcopyrite at different pulp potentials, the surface of chalcopyrite is characterized in the presence of sodium sulfide using X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Sample preparation

Experiments were conducted using single minerals of chalcopyrite as well as chalcopyrite flotation concentrate samples. The chalcopyrite flotation concentrate samples were obtained from the Sarcheshmeh Copper Complex Concentrator and the single mineral samples were hand selected from high-grade lump materials obtained from the Sarchrshmeh Copper Mine. The lumps were crushed to below 15 mm in a laboratory jaw crusher. They were then ground to below 100 μm with a laboratory ceramic ball mill from which particle sizes below 37 μm were removed. Afterwards, the samples were stored in sealed polyethylene bags. A 75 μm particle size, d_{80}, was measured for both sample types.

Calculated from chemical analysis and mineralogical observations, the chemical composition and mineralogical composition of the samples are given in Tables 1 and 2, respectively. Element content was measured by atomic absorption spectroscopy (AAS-Varian, model A 220) and X-ray fluorescence (XRF-Philips, model PW 1480). Mineralogical studies were carried out using an optical microscope with relevant software to count and calculate the percentage of minerals according to results from the chemical analysis.

Table 1. Chemical assays of the samples wt%

Sample	Cu	Fe	CaO	Al_2O_3	K_2O	SiO_2	S	Others
Single Chalcopyrite	34.16	30.08	0.02	0.22	0.05	0.36	34.46	0.65
Chalcopyrite Concentrate	27.22	25.79	0.57	—	—	5.19	33.86	7.37

Table 2. Mineralogical composition of the samples wt%

Sample	Chalcopyrite	Pyrite	Chalcocite	Covellite	Bornite	Other Minerals
Single Chalcopyrite	97.37	0.95	0	0.37	0.09	1.22
Chalcopyrite Concentrate	47.85	24.02	6.65	6.27	0.98	14.23

2.2. Reagents

All used chemicals were analytical grade. The reagents were: sodium sulfide ($Na_2S·9H_2O$), polypropylene oxide methanol (Dowfroth 250) as a frother, phosphate base buffer solution consisting of phosphoric acid (H_3PO_4) and sodium hydroxide (NaOH), and hydrogen peroxide (H_2O_2) as an oxidizing agent.

2.3. Fourier transform infrared (FTIR) measurements

0.5 g of the powdered chalcopyrite samples were suspended in solutions with a desired reagent concentration. The suspensions were stirred and then left to settle completely. The samples were then filtered, dried, and then mixed with purified fine potassium bromide salt (KBr). The mixture was then pressed into a pellet for FTIR measurements. The FTIR spectra of the samples were recorded using a Tensor 27 (Brucker Company) spectrophotometer.

2.4. XPS measurements

All samples were prepared at the desired conditions described in section 3 and stored in liquid nitrogen to prevent extra oxidation. XPS measurements were carried out with a physical electronics (Specs Company, model EA10 Plus) spectrometer using an Al K_α X-ray source operating at 150 W. The pressure in the analysis chamber was 1.33×10^{-7} Pa during analysis. All spectra were calibrated using the carbon 1s spectral peak which has a known position of 284.6 eV.

2.5. Procedure

The single mineral flotation tests were conducted in a 150 mL microflotation cell (Fig. 1). The flotation concentrate tests were carried out in a conventional laboratory Denver cell. In all tests depending on desired pulp potential, purified nitrogen, air or oxygen gas were bubbled into the cells and in some cases the pulp potential was controlled by adding hydrogen peroxide (H_2O_2). Flotation tests were conducted at various pulp potential (E_h) values and sodium sulfide concentration ranging from 10^{-1} to 10^{-4} mol/L at a pH value of 12. Sodium sulfide drives the pulp to alkaline pH values, so in this study pH 12 was investigated. The pH value and E_h were monitored continuously throughout each flotation test. The pH value was measured using a glass electrode (model Metrohm 826). A phosphate base buffer solution was used to maintain a pH value of 12 ± 0.5. The working and reference electrodes used to monitor the pulp potential were Pt and Ag-AgCl (3 M KCl solution, model WTW 325), respectively, and were reported as SHE. The performance of the E_h electrode was checked using a standard ferric-ferrous solution [23]. The recovery percent for the single mineral tests was calculated based on the mass of the mineral recovered and the total mass of particles in the original feed. Entrainment was assumed to be relatively low and has not been subtracted from these results. The recovery percent for the flotation concentrate tests was also calculated based on the recovery relationship,

$$R = \frac{cC}{fF} \times 100\%,$$

where c, C, f, and F are the grade of chalcopyrite in the concentrate, mass of concentrate, grade of chalcopyrite in the feed, and the mass of feed, respectively.

In each series, three tests were conducted at selected conditions to ensure appropriate reproducibility. The deviation of the recovery values obtained from repeated experiments did not exceed ±2%.

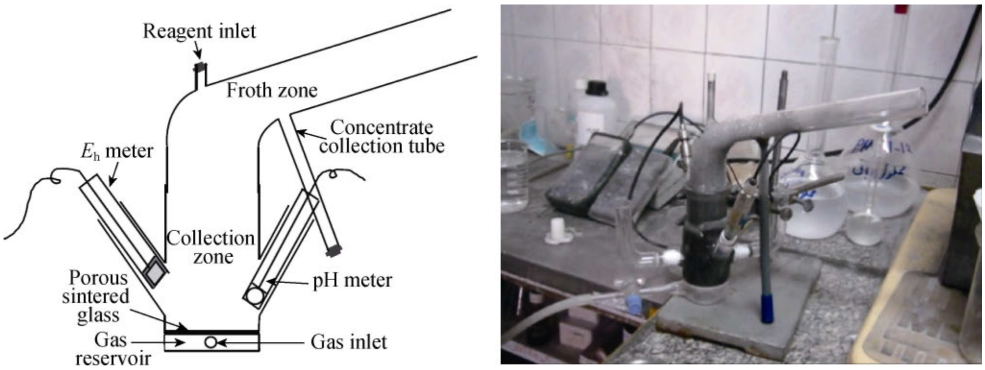

Fig. 1. Schematic representation of the microflotation cell.

3. Results and discussion

Fig. 2 shows the flotation recovery of chalcopyrite as a function of E_h at different concentrations of sodium sulfide. In both single chalcopyrite (a) and chalcopyrite flotation concentrate (b) experiments, at the higher concentrations of sodium sulfide, especially at 10^{-1} mol/L and 10^{-2} mol/L, maximum depression of chalcopyrite occurred in a specific range of pulp potential. At the initial potential, after adding sodium sulfide to the pulp, chalcopyrite was not immediately depressed. By increasing the potential, chalcopyrite began to be depressed and maximum depression occurred in the range of approximately −200 mV to −100 mV. This suggests that a partial and controlled oxidation of pulp may be necessary to ensure maximum depression of chalcopyrite flotation. At potentials of more than 0 mV, the flotation recovery of chalcopyrite increased for all sodium sulfide concentrations.

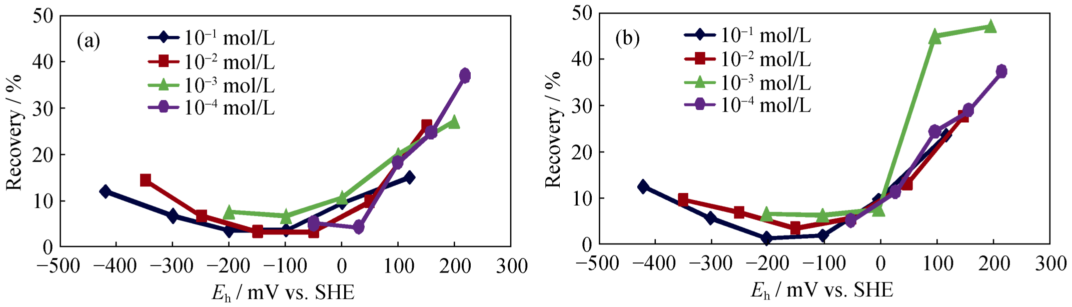

Fig. 2. Recovery of chalcopyrite as a function of E_h at pH 12 and at different concentrations of sodium sulfide: (a) single chalcopyrite; (b) chalcopyrite concentrate.

The desorption of collectors from the mineral surfaces has been previously reported [1,10] as the depression mechanism of sodium sulfide in sulfide minerals. This study confirmed these reports using FTIR spectroscopy. As shown in Fig. 3, approximately all peaks related to collector-chalcopyrite bands (1275, 1190, 1151, 1125, 1035, and 1005

cm^{-1}) [11,24–25] have disappeared after conditioning chalcopyrite in a 10^{-2} mol/L sodium sulfide solution.

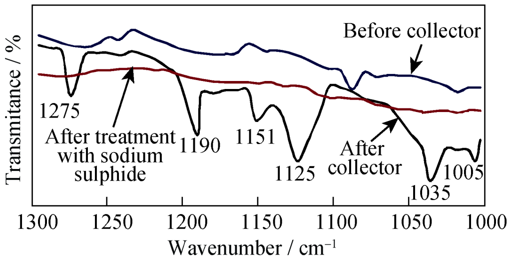

Fig. 3. FTIR spectra of collector (10^{-3} mol/L potassium ethyl xanthate) treated chalcopyrite before and after conditioning with sodium sulfide (10^{-2} mol/L).

It appears that the adsorption of sodium sulfide on the chalcopyrite surface and desorption of collectors from the surface do not fully depress chalcopyrite. To completely depress chalcopyrite with sodium sulfide, a hydrophilic species should be formed. It has been shown [26] that sodium sulfide can react with oxygen to form a sulphoxy species such as thiosulfate ($S_2O_3^{2-}$), sulphite (SO_3^{2-}), and sulfate (SO_4^{2-}). Metastable elemental sulfur has also been found [27] in sodium sulfide-water solutions. McCarron *et al.* [28] discovered multilayer quantities of elemental sulfur on the surface of chalcopyrite which had been conditioned in sodium sulfide solutions. Sulphoxy and elemental sulfur are hydrophilic and hydrophobic species, respectively [19,29]. In sodium sulfide solutions, these species may form and adsorb on the mineral surface causing them to be depressed or float during flotation processes.

These reports suggest that under these conditions a relatively high recovery of chalcopyrite at initial potentials (Fig. 1) may be due to the hydrophobic metastable elemental sulfur or polysulfide species resulting from the electrochemical interactions of Na_2S in the pulp or an inadequate hydrophilic species on the mineral surface. Alternatively, the reactions resulting from chalcopyrite in alkaline solutions may also produce hydrophobic and hydrophilic species as follows [13,27,30]:

$$CuFeS_2 + 3H_2O = CuS + Fe(OH)_3 + S + 3H^+ + 3e^- \quad (2)$$

$$2CuFeS_2 + 9H_2O = 2CuS + 2Fe(OH)_3 + S_2O_3^{2-} + 12H^+ + 10e^- \quad (3)$$

$$2CuS + 7H_2O = 2Cu(OH)_2 + S_2O_3^{2-} + 10H^+ + 8e^- \quad (4)$$

$$CuS + 2H_2O = Cu(OH)_2 + S + 2H^+ + 2e^- \quad (5)$$

Hydrophilic metal hydroxides and sulphoxy species resulting from the above reactions may also have depressing effects on chalcopyrite. In contrast, hydrophobic entities such as elemental sulfur and sulfur rich metal deficient compounds (CuS) produced as chalcopyrite oxidation products may also cause the flotation of chalcopyrite. However, in the flotation concentrate experiments, electrochemical side reactions occurring from other minerals in solution or galvanic interactions between different minerals make it difficult to predict the hydrophilic or hydrophobic species responsible for the depression and flotation of chalcopyrite. Therefore, X-ray photoelectron spectroscopy (XPS) was used to identify the species formed on surface of chalcopyrite. The S (2p), Fe ($2p_{3/2}$), and Cu (2p) XPS spectra of chalcopyrite minerals conditioned at pH 12 in a Na_2S solution (10^{-1} mol/L) and at different potentials (−420, −300, −200, 0, and +100 mV) were analyzed to characterize the species formed on the particles in the flotation processes (Figs. 4–8). According to previous studies [31–37], the peaks around 160 to 164 eV of the S (2p) spectra represent hydrophobic species such as bulk disulphur, polysulfide, elemental sulfur, or higher order polysulfides. The peaks around 168 eV are representative of hydrophilic sulphoxy species (sulfate, thiosulfate). In the Fe ($2p_{3/2}$) spectra, the peaks around 710–713 eV and 724–726 eV represent iron oxide/hydroxide hydrophilic species, while the peaks around 708 eV are related to iron associated with S (FeS or $CuFeS_2$). The peaks around 934, 935, and 942 eV in the Cu (2p) spectra represent hydrophilic copper oxide or hydroxide species, while the peaks around 932 and 952 eV represent hydrophobic CuS species.

Fig. 4 illustrates the S (2p), Fe ($2p_{3/2}$), and Cu (2p) XPS spectra of the chalcopyrite sample conditioned at pH 12, 10^{-1} mol/L Na_2S, and $E_h = -420$ mV. As it is shown, there is a peak between 161 to 162 eV and a slight peak at 164 eV in S (2p) spectra which are related to hydrophobic sulfur species. The peaks around 708 eV in Fe ($2p_{3/2}$) and at 932 and 952 eV in Cu (2p) may relate to chalcopyrite structure. A broad peak around 720 eV in Fe ($2p_{3/2}$) may consists of hydrophilic iron hydroxide species. It seems that both hydrophobic and hydrophilic species are present at the surface at $E_h = -420$ mV, but the relatively high floatability of chalcopyrite at this condition may be due to the hydrophobic sulfur species. Thus, elemental sulfur or other hydrophobic species may be responsible for the flotation of chalcopyrite at initial potentials.

At pH 12, 10^{-1} mol/L Na_2S, and $E_h = -300$ mV, shown in Fig. 5, the peaks related to hydrophilic sulphoxy species (168–170 eV) have appeared in the S (2p) spectra, and in the Fe ($2p_{3/2}$) spectra small peaks that may be related to iron oxide/hydroxide have partially appeared. In the Cu (2p) spectra, a copper hydroxide related peak has appeared around 935 eV. It seems that the coexistence of these hydrophilic species results in the lower recovery of chalcopyrite at $E_h = -300$ mV.

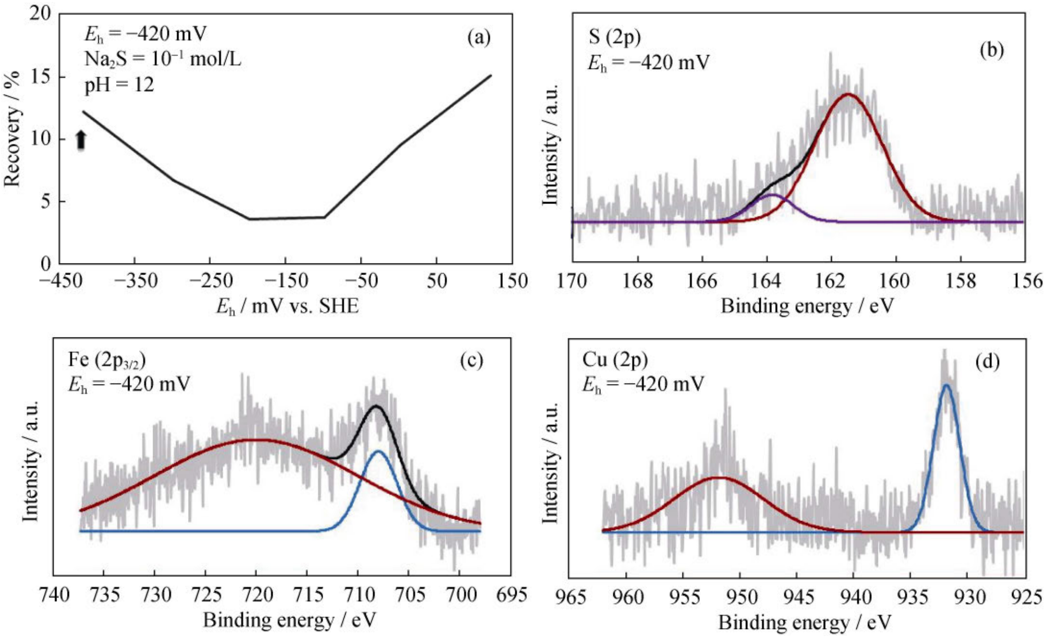

Fig. 4. Flotation result (a) and XPS spectra (b, c, and d) of the chalcopyrite surface after being conditioned in 10^{-1} mol/L Na_2S at pH 12 and E_h = −420 mV: (b) S (2p); (c) Fe ($2p_{3/2}$); (d) Cu (2p).

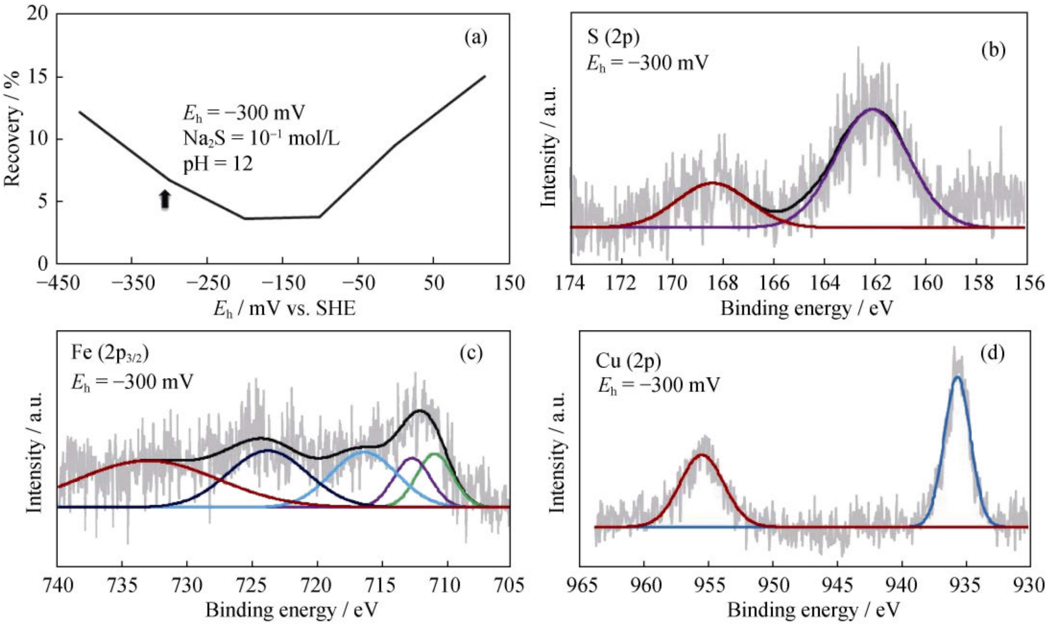

Fig. 5. Flotation result (a) and XPS spectra (b, c, and d) of the chalcopyrite surface after being conditioned in 10^{-1} mol/L Na_2S at pH 12 and E_h = −300 mV: (b) S (2p); (c) Fe ($2p_{3/2}$); (d) Cu (2p).

Fig. 6 shows the S (2p), Fe ($2p_{3/2}$), and Cu (2p) XPS spectra of the chalcopyrite sample prepared at pH 12, E_h = −200 mV, and 10^{-1} mol/L Na_2S, in which the maximum depression of chalcopyrite occurred. The sulfide hydrophobic species have decreased while the hydrophilic sulphoxy species have simultaneously increased relative to previous conditions (E_h = −420 mV and −300 mV). In the Fe ($2p_{3/2}$) spectra hydrophilic iron oxide/hydroxides species appear to be present at the mineral surface. In the Cu (2p) spectra, a new peak appears at 942 eV, which is related to copper oxide or hydroxide hydrophilic species. All these hydrophilic species may cause chalcopyrite to be appropriately depressed under this condition.

As previously stated, the flotation recovery of chalcopyrite increases slowly with increasing potential in the range of 0 to +100 mV, while other conditions are kept constant (pH

12 and 10^{-1} mol/L Na_2S). The S (2p), Fe ($2p_{3/2}$), and Cu (2p) XPS spectra of chalcopyrite samples at E_h = 0 mV are shown in Fig. 7. At E_h = 0 mV, although the iron oxide/hydroxide peaks are partially present, the peaks related to hydrophobic sulfide species (161 to 164 eV) have increased in relation to previous conditions (Fig. 6). However, the peak at 942 eV in the Cu (2p) spectra has a lower intensity relative to previous conditions (E_h = −200 mV). These phenomena may be responsible for the increased chalcopyrite flotation under these conditions.

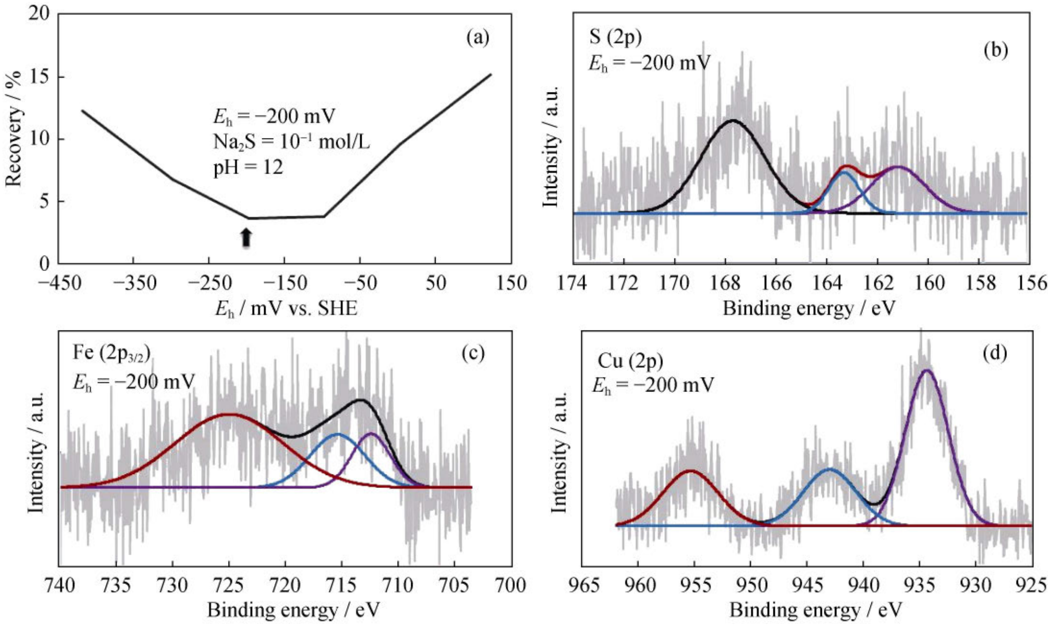

Fig. 6. Flotation result (a) and XPS spectra (b, c and d) of the chalcopyrite surface after being conditioned in 10^{-1} mol/L Na_2S at pH 12 and E_h = −200 mV: (b) S (2p); (c) Fe ($2p_{3/2}$); (d) Cu (2p).

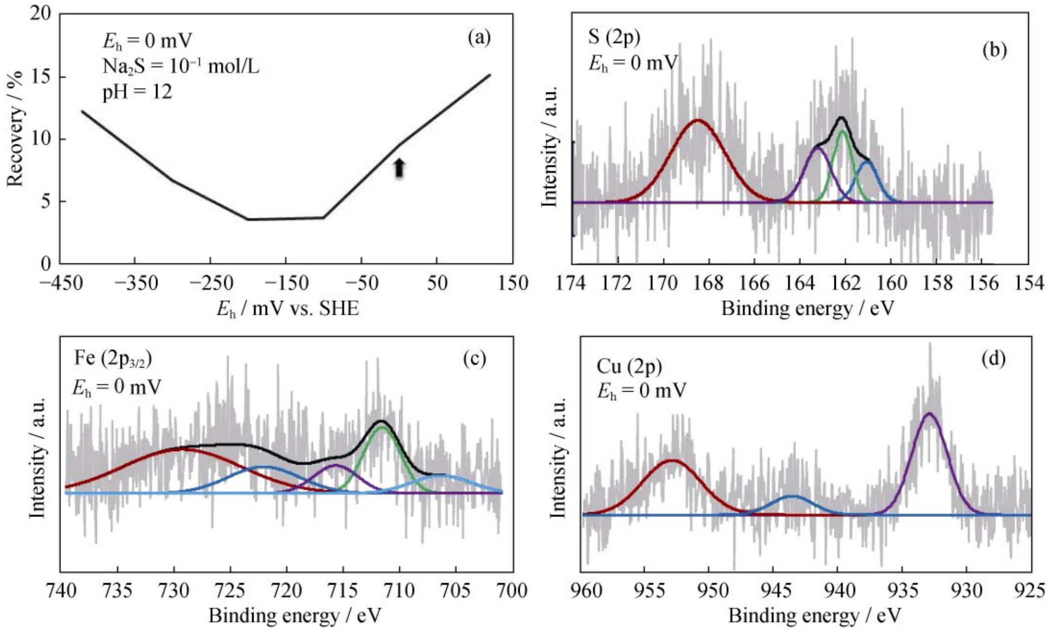

Fig. 7. Flotation result (a) and XPS spectra (b, c, and d) of the chalcopyrite surface after being conditioned in 10^{-1} mol/L Na_2S at pH 12 and E_h = 0 mV: (b) S (2p); (c) Fe ($2p_{3/2}$); (d) Cu (2p).

At E_h = +100 mV (Fig. 8), where the flotation recovery of chalcopyrite significantly increased, both sulfide hydrophobic and hydrophilic species are present in the S (2p) spectra. In contrast with potential E_h = 0, it seems that the hydrophobic sulfide and hydrophilic sulphoxy species have increased and decreased, respectively. Despite the presence of iron oxide/hydroxide species in the Fe ($2p_{3/2}$) spectra, the peak at 942 eV in the Cu (2p) spectra, attributed to hydrophilic copper hydroxide species, has almost disappeared. These phenomena may cause an increase in the flotation recovery of chalcopyrite at E_h = +100 mV. The increasing recovery of chalcopyrite with increasing potential from 0 to 100 mV is likely due to the activating effect of sodium sulfide as a sulphidizing agent. It seems that metastable elemental sulfur forms and adsorbs strongly on chalcopyrite particles as they are formed in the pulp, and gets more stable on the mineral surfaces resulting in hydrophobic surfaces. Thus, sulfate ions or other hydrophilic species such as metal hydroxides may not fully depress chalcopyrite.

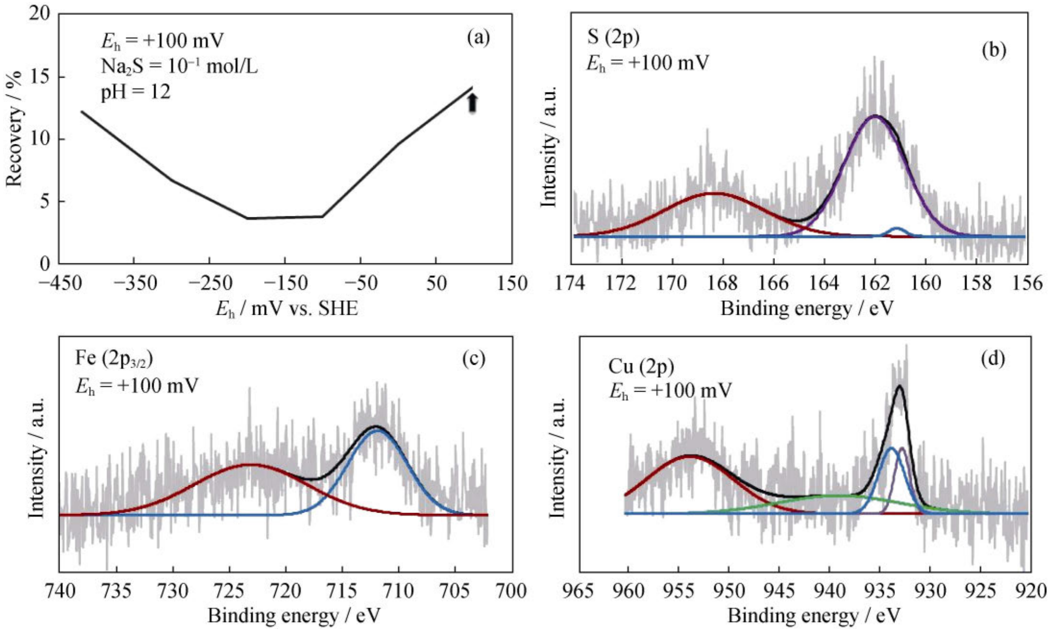

Fig. 8. Flotation result (a) and XPS spectra (b, c, and d) of the chalcopyrite surface after being conditioned in 10^{-1} mol/L Na_2S at pH 12 and E_h = +100 mV: (b) S (2p); (c) Fe ($2p_{3/2}$); (d) Cu (2p).

4. Conclusions

(1) The dual effects of sodium sulfide on the flotation behavior of chalcopyrite are highly dependent on the pulp potential.

(2) A partial and controlled oxidation of pulp may be necessary to ensure the maximum depression of chalcopyrite flotation after adding Na_2S to the pulp.

(3) Elemental sulfur and sulphoxy species are produced from electrochemical interactions between sodium sulfide and pulp contents. Those species along with oxidation–reduction products from chalcopyrite strongly affect the floatability of chalcopyrite.

(4) Stable or metastable elemental sulfur adsorbed by chalcopyrite particles forming in the pulp makes the chalcopyrite surfaces hydrophobic.

(5) Only through the coexistence of sulphoxy and hydrophilic iron or copper oxide/hydroxide species can overcome the hydrophobicity of chalcopyrite surfaces and make them hydrophilic.

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