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Influence of the Interaction between Sphalerite and Pyrite on the Copper Activation of Sphalerite

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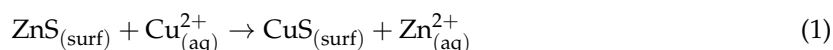
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Abstract: In this paper, the effect of pyrite on the activation of sphalerite was investigated by micro-flotation, copper adsorption experiments, X-ray photoelectron spectroscopy (XPS), and electrochemical measurement. The micro-flotation test results showed that the recovery and flotation rate of sphalerite with copper sulphate as activator and butyl xanthate as collector were significantly decreased with the increasing content of pyrite in pulp. Cu²⁺ adsorption results indicated that the adsorption of Cu²⁺ on the sphalerite surface were decreased when pyrite was present in the pulp. XPS surface analysis demonstrated that the proportion of Cu⁺ species increased in the activation products on the sphalerite surface, but the total atomic concentration of Cu atom was decreased. Linear voltammetry measurement suggested that the current density of Cu⁺ species oxidizing to Cu²⁺ species was increased when sphalerite was electrically contacted with pyrite, which confirmed the increased proportion of Cu⁺ species on Cu-activation sphalerite surface when contacting with pyrite. These results indicated that there is not only a competitive adsorption for cupric ions (Cu²⁺), but the galvanic interaction between sphalerite and pyrite also has a significant influence on the copper activation of sphalerite.

Keywords: Cu activation; sphalerite; interaction between minerals; pyrite

1. Introduction

Sphalerite is an important resource for zinc metal production, and selective separation of sphalerite from its associated sulfide minerals is commonly carried out by froth flotation [1–3]. During the selective flotation of sphalerite, copper sulfate (CuSO₄) is often used as activator to improve flotation performance. [4–6]. The copper activation of sphalerite follows an ion exchange reaction, and the uptake of Cu²⁺ from the solution results in an approximately 1:1 release of Zn²⁺ into the solution. This reaction is represented by the following equation [7]:



Then, Cu²⁺ adsorbed on the sphalerite surface is reduced to Cu⁺ accompanied by the oxidation of the surface S²⁻ to S⁰ or S_n²⁻.

Pyrite, a common sulfide gangue mineral, is usually associated with sphalerite. During the selective flotation of sphalerite, pyrite is usually depressed by using lime. In alkaline pH ranges, pyrite surface is more hydrophilic than in acidic or neutral pH ranges due to the formation and adsorption of Fe-hydroxide complexes on the surface [8,9]. However, it has been proved that the flotation of pyrite can be activated by heavy metal ions, such as Cu²⁺ and Pb²⁺, even in alkaline pH ranges. During

pyrite activation, metal ions are precipitated or adsorbed on the mineral surface to create suitable sites for the adsorption of the collector [10,11]. In the selective flotation of sphalerite, the undesired activation of pyrite will reduce the difference in flotation performance between sphalerite and pyrite, and cause a decrease in the recovery and grade of Zn concentrates.

However, a number of studies on the Cu activation of sphalerite and pyrite have been conducted in single mineral systems, where only a competitive adsorption for Cu^{2+} ions and xanthates between sphalerite and pyrite was considered as the reason for the difficulty in the selective separation of sphalerite from pyrite [11,12]. It has been suggested that the galvanic interaction between sulfide minerals has an important influence on the selective separation and surface characteristics of mineral [13,14]. Results from Owusu's studies indicated that the flotation rate, recovery, and grade of chalcopyrite decreased with increasing pyrite content in feed [15–17]. Qin et al. studied the interaction between galena and pyrite, and results from their research indicated that pyrite did not change the oxidative and reductive products on the surface of galena, but it increased the current density and oxidation rate during galena oxidation. Consequently, the floatability of galena and pyrite decreases and increases, respectively [18]. Majid Ejtemaei and Anh V. Nguyen used high-speed video microscopy (HSVM) and studied the effect of pyrite on CuSO_4 activation and xanthate adsorption of the sphalerite surface. Their results showed that CuSO_4 activation rate and xanthate adsorption rate of the sphalerite significantly dropped with the increasing ratio of sphalerite to pyrite surface areas exposed to CuSO_4 solution, but the activation rate was unchanged when the ratio of surface areas was equal to 1:1 [19,20].

In industrial practices, the Yiliang Pb-Zn deposits in Southwest China are regarded as the richest lead and zinc ores in China. The grades of Pb, Zn, and S are 7.8%, 18.4%, and 34.8%, respectively, and the pyrite and sphalerite content in the ores are respectively 51.3% and 27.3%. However, the recovery and grade of Zn concentrate only reaches 88.3% and 48.7% due to the influence of pyrite in selective flotation. On the other hand, in order to achieve successful flotation of sphalerite, a large amount of activator copper sulfate and collector butyl xanthate (BX) are used. In addition, exploitable ores are mostly found as an association of sulfide minerals, and the flotation behavior of a single mineral is different from mixed minerals [21,22]. The rest potential for the common sulfide minerals are classified in an increasing order as follows: $\text{ZnS} < \text{PbS} < \text{CuFeS}_2 < \text{FeS}_2$. From the viewpoint of electrochemistry, the difference in rest potential is an important driving force that promotes the transfer of electrons between minerals [23]. Therefore, a study on the effect of interaction between sphalerite and pyrite on the Cu activation of sphalerite is meaningful to further understand the reason for difficulty in the selective flotation of sphalerite from the associated pyrite. In this paper, micro-flotation tests, adsorption measurement, X-ray photoelectron spectroscopy (XPS) analysis, and voltammetry measurement were used to further investigate the influence of the interaction between sphalerite and pyrite on the copper activation of sphalerite.

2. Materials and Methods

2.1. Minerals

The highly-mineralized sphalerite and pyrite samples used in this study were obtained from Yiliang Mine, Yunnan Province, China. After the manual removal of gangue minerals, such as quartz and calcite, the samples were dry-ground in a porcelain ball mill and dry-screened using nylon sieves to obtain the desired particle size. The sample was prepared just prior to its use in order to prevent surface oxidation. The chemical compositions of sphalerite and pyrite samples were quantified by atomic absorption spectrophotometer (AAS) using a Perkin Elmer model 2000 analyzer after acid digestion, and the results are listed in Table 1. X-ray diffraction analysis (D/Max 2200, Rigaku, Tokyo Japan) showed that the samples used in this study were of high purity.

Table 1. Chemical compositions of sphalerite and pyrite samples.

Elements	Zn	Fe	S	Pb	SiO ₂
Sphalerite	63.26	1.04	33.25	0.43	0.93
Pyrite	0.006	53.26	46.16	0.21	0.22

2.2. Procedure

2.2.1. Flotation Tests

Flotation tests were conducted in a 40 mL flotation cell with 4.0 g of $-0.106/+0.075$ mm sphalerite or pyrite sample for each test. In the mixture mineral tests, 4.0 g mineral mixtures with different proportions of sphalerite and pyrite were used. The sample was first mixed with 40 mL deionized water, and the pH of the pulp was adjusted to a specified pH by using 0.01 mol/L HCl and NaOH solution. After that, analytical grade CuSO₄ and industrial grade butyl xanthate (BX) were added and conditioned for 3 min and 2 min, respectively. Then, the frother methyl isobutyl carbinol (MIBC) was added and conditioned for 1 minute. Finally, the slurry was floated for 3 min, and the floated particles were collected at different intervals, dried, and assayed for the calculation of recovery. All the tests were repeated three times under the same conditions; the recovery reported in this paper is the average of the three tests.

2.2.2. Copper Adsorption

The conditions used in adsorption tests were the same as for flotation. Firstly, sphalerite or pyrite or a mixture of both were added to a 100 mL reaction vessel with 40 mL deionized water, and the pH of the suspension was adjusted with HCl and NaOH solutions. Then, a specified dosage of CuSO₄ was added and a magnetic stirrer was used for stirring the suspension at a speed of 800 rpm for 5 min. At the end of stirring, the suspension was separated by using a centrifuge at 3500 rpm for 5 min. After separation, the aqueous solution was subjected to Cu²⁺ and Zn²⁺ concentration analysis by using an inductively coupled plasma emission spectrometer (ICPS-1000II, Shimadzu, Kyoto, Japan). The solid particles were quickly added to a 3% ethylene diamino tetraacetic acid (EDTA) solution for extraction of the Cu²⁺ and Zn²⁺ ions adsorbed on the mineral surface. Before EDTA addition, the EDTA solution was bubbled with nitrogen gas with 99.99% purity for 30 min. During EDTA extraction, nitrogen was continuously purged with a lower flow rate to prevent further oxidation of the mineral surface.

2.2.3. Analysis Techniques

An X-ray photoelectron spectrometer (PHI5000, ULVAC-PHI, Kanagawa, Japan) was used to identify the elements and chemical status of the Cu-activated sphalerite surface. The samples were prepared by the following procedure. The $0.6 \times 0.6 \times 0.2$ cm sphalerite block was wet-polished with 1200 grit polishing paper for 2 min. Then, the sample was washed with deionized water and immersed quickly in a suspension containing either 1.0 g of -0.048 mm pyrite or no pyrite. The surface subjected to XPS analysis was exposed to the suspension, and a specified dosage of CuSO₄ was added into the suspension. After stirring for 10 min using a shaking table, the sphalerite block was taken and washed with deionized water with the same pH, and dried in a vacuum environment. After that, XPS measurements were taken.

The voltammetry measurement was carried out using an electrochemical workstation (Zahner IM 6, Kansas City, MO, USA). The traditional electrode system was used, consisting of a working electrode (mineral electrode), a counter electrode (platinum electrode with an area of 1 cm²) and a reference electrode (Ag/AgCl electrode, 3.0 mol/L KCl). The working electrode of sphalerite was prepared by the method described by Urbano and Chen [5,24]. To simulate the mixed mineral system, the working electrode was first immersed in the solution containing 1.0 g pyrite and 2.0×10^{-4} mol/L

CuSO_4 for activation for 10 min. After activation, the working electrode was quickly transferred to the cell for electrochemical measurements. The solution used in the electrochemical tests was bubbled with 99.99% pure nitrogen gas for 30 min. No CuSO_4 was added in the electrochemical tests.

3. Results and Discussion

3.1. Flotation Behavior of Sphalerite with and without the Presence of Pyrite

Flotation tests were carried out to investigate the influence of pyrite on the flotation behavior of sphalerite with CuSO_4 as the activator and butyl xanthate as the collector. The flotation recovery of sphalerite alone, and mixed with different proportions of pyrite, as a function of pH and flotation time are shown Figure 1.

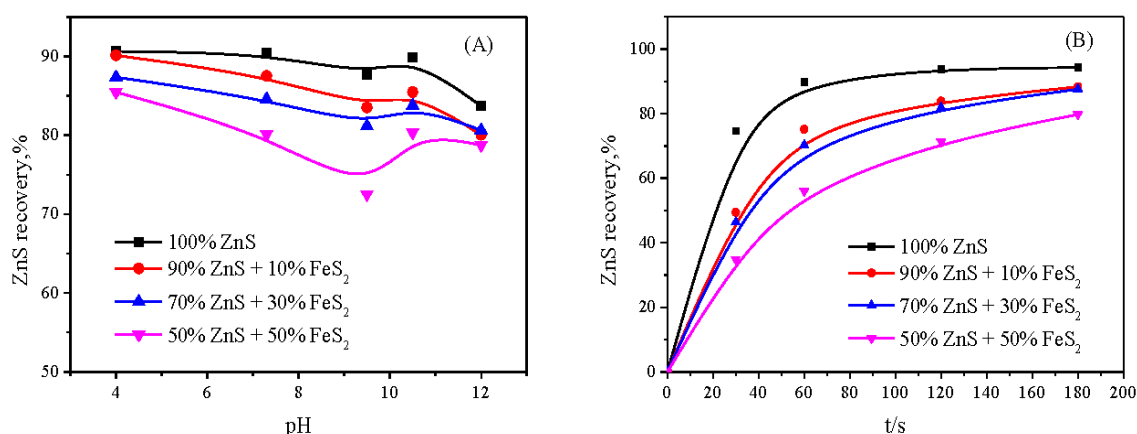


Figure 1. Influence of pyrite on the flotation behavior of sphalerite at different pH and flotation time, 2.0×10^{-4} mol/L CuSO_4 , 10 mg/L butyl xanthate, (A) recovery of sphalerite, (B) flotation rate of sphalerite.

It is evident from Figure 1 that the flotation behavior of sphalerite in a pyrite mixture was different from that of the sphalerite alone. The recovery of sphalerite in the mixture was lower at all of the studied pH levels compared to the sphalerite alone. In the alkaline pH ranges of 8 to 11, the decrease in sphalerite recovery was approximately 20%. In addition, the flotation rate of sphalerite at a pH of 9.5 was significantly lower with increasing pyrite content in the mixture compared to sphalerite alone.

The decrease in recovery and flotation rate of sphalerite mixed with pyrite can be attributed to the galvanic interaction between sphalerite and pyrite. Qin and Wang [25] suggested that the galvanic interaction between sulfide minerals has an important influence on the flotation response of sulfide minerals and the redox reaction that occurs on the mineral surface. Between sphalerite and pyrite, pyrite possesses the highest rest potential; the rest potential of sphalerite is relatively low [23]. Accordingly, the surface oxidation of sphalerite and pyrite will be increased and inhibited, respectively, after galvanic interaction. On the other hand, the competitive adsorption for Cu^{2+} and xanthate may be another important factor causing the decrease in the recovery and flotation rate of sphalerite [12].

3.2. Copper Adsorption

The activation of sphalerite was conducted with CuSO_4 as the activator, both in the absence and presence of pyrite, to investigate the influence of pyrite on copper activation of sphalerite, and the results are shown in Figure 2. In Figure 2, the y-axis represents the difference in Cu^{2+} concentrations before and after adsorption. The higher the values of $C_0 - C_t$, the more Cu^{2+} ions were adsorbed on the mineral surface.

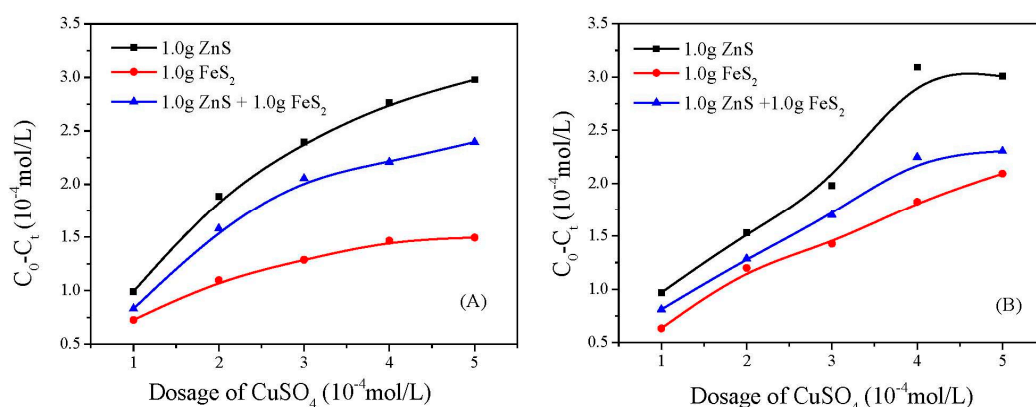


Figure 2. Adsorption capacity of Cu^{2+} on sphalerite surface with and without the presence of pyrite, (A) pH = 7.3, (B) pH = 9.5.

For sphalerite or pyrite alone, the adsorption capacity of Cu^{2+} on the mineral surface increased with increasing dosages of CuSO_4 under pH values of 7.3 and 9.5, and the adsorption capacity of Cu^{2+} on the sphalerite surface was higher than that on the pyrite surface. The adsorption capacity of Cu^{2+} on the sphalerite surface was fully saturated at a pH of 7.3 when CuSO_4 reached a concentration of 4×10^{-4} mol/L. Compared to the sphalerite alone, however, an obvious decrease in Cu^{2+} concentrations before and after adsorption was observed when 1.0 g pyrite was present in the pulp. If there is only a competitive adsorption between sphalerite and pyrite for Cu^{2+} , the Cu^{2+} concentration difference in the both sphalerite and pyrite condition should surpass the Cu^{2+} concentration difference with sphalerite alone, especially when using a higher dosage of CuSO_4 , (e.g., 4.0×10^{-4} mol/L). The results from Figure 2 indicate that the presence of pyrite in pulp has a significant influence on the copper activation of sphalerite, which leads to a decrease in the adsorption capacity of Cu^{2+} on the sphalerite surface. It has been proven that the copper activation of sphalerite can be expressed by an ion exchange reaction, and the uptake of Cu^{2+} from the solution results in an approximately 1:1 release of Zn^{2+} into the solution [7]. Therefore, in order to further investigate the influence of pyrite on the copper activation of sphalerite, the concentration of Zn^{2+} in solution and adsorbed on the mineral surface was considered. A 3% EDTA solution was used to extract the Zn^{2+} adsorbed on mineral surface. The total amount of Zn^{2+} released from the sphalerite surface or lattice was calculated by adding the Zn^{2+} concentration in solution and the EDTA extractable Zn^{2+} from the mineral surface. The results are shown in Figure 3.

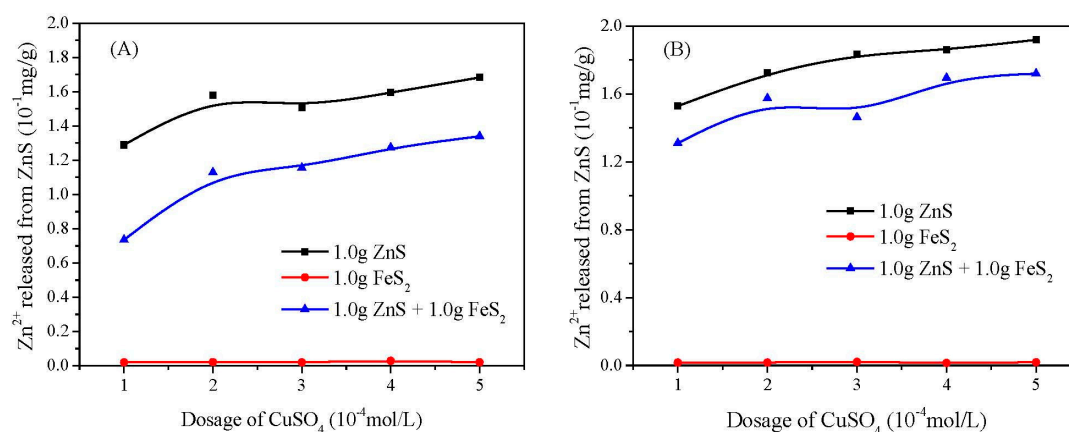


Figure 3. The total amount of Zn^{2+} released from the sphalerite surface or lattice. (A) pH = 7.3, (B) pH = 9.5.

Figure 3 indicates that the Zn^{2+} ions released from the sphalerite surface or lattice increased with increasing the dosage of $CuSO_4$ for sphalerite alone and the mixture, but for the mixed minerals system, the Zn^{2+} concentration significantly decreased when pyrite was present in the pulp. These results are consistent with the results in Figure 2, which further confirms that the both sphalerite and pyrite not only exists a competitive adsorption for Cu^{2+} in solution, but also the presence of pyrite in pulp has a significant influence on the copper adsorption of sphalerite surface. Majid Ejtemaei and Anh V. Nguyen have demonstrated that during the $CuSO_4$ activation of sphalerite, the activation rate of sphalerite significantly dropped with the increasing ratio of pyrite to sphalerite surface areas exposed to $CuSO_4$ solution. The decrease in Cu^{2+} adsorption kinetics of sphalerite surface may be the important reason for the mixed minerals system [20]. Some studies have found that the electrochemical interaction between sulfide minerals has an important influence on the surface reactivity of sulfide minerals [24,25]. The galvanic interaction between sphalerite and pyrite may be another critical factor affecting the adsorption of Cu^{2+} on sphalerite surfaces.

3.3. XPS Study

The surface XPS analysis of sphalerite activated by $CuSO_4$ —both in the presence and absence of pyrite in the pulp—was carried out, and the high-resolution Cu 2p scanning results are shown in Figure 4.

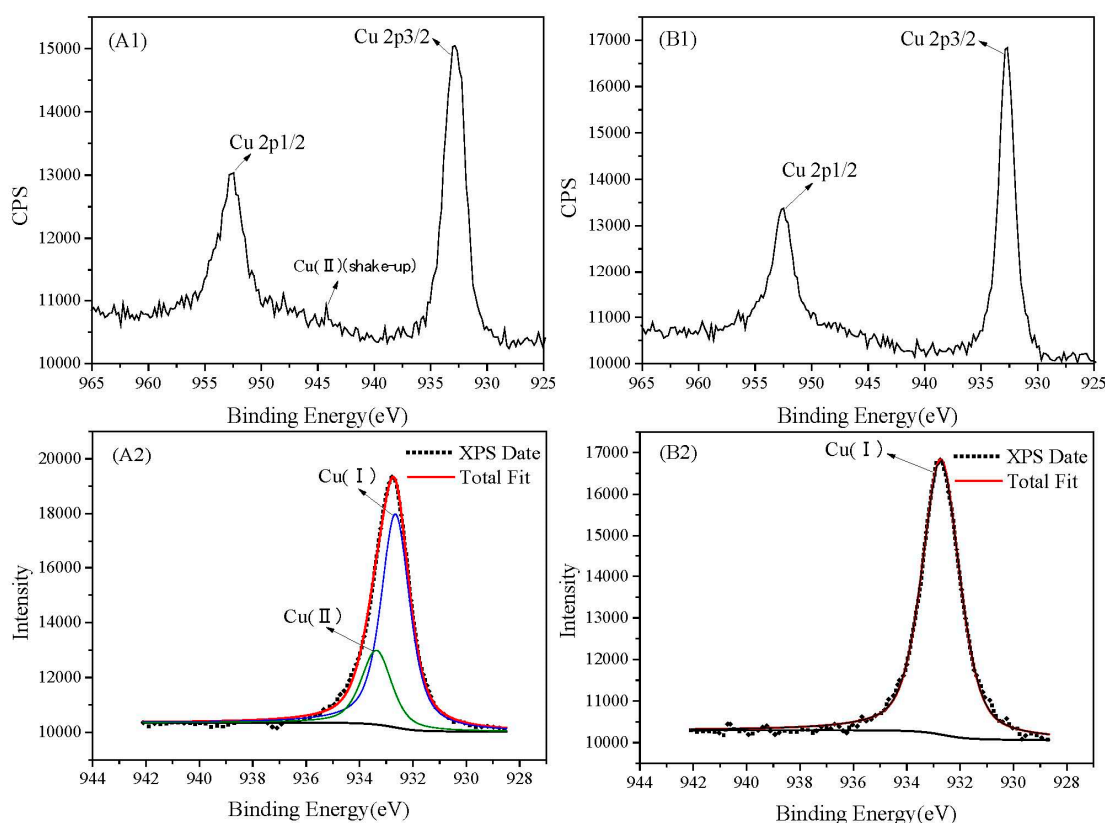


Figure 4. Cu 2p spectra of sphalerite activated with 2.0×10^{-4} mol/L of $CuSO_4$ at a pH of 7.3, the Cu 2p (A1) and the fitting Cu2p3/2 (A2) of sphalerite alone, the Cu 2p (B1) and the fitting Cu2p3/2 (B2) of sphalerite in the presence of pyrite.

Figure 4 demonstrates the Cu 2p spectra of sphalerite activated by $CuSO_4$ with and without the presence of pyrite in the pulp. In Figure 4(A2), Cu 2p3/2, with a binding energy of 932.3 eV, was attributed to Cu^+ from the activation products of the sphalerite surface. The Cu 2p3/2 at binding energy of 933.4 eV was considered as the Cu^{2+} species formed by copper hydroxide precipitation on the

sphalerite surface. These results are consistent with those of Fornasiero and Ejtemaei [6,26]. The Cu^+ and Cu^{2+} species are the main activation product occurring on the sphalerite surface. Compared to Figure 4A, however, the Cu 2p3/2 of Cu^{2+} almost disappeared when pyrite was present in the pulp (Figure 4(B2)). This finding is interesting, as it indicates that the interaction between sphalerite and pyrite in pulp affects the activation products and the reduction of Cu^{2+} to Cu^+ species on the sphalerite surface.

In order to further investigate the effect of the interaction between sphalerite and pyrite on the activation products on the sphalerite surface, a high-resolution scan of S 2p was carried out, and the results are shown in Figure 5. Many studies have suggested that S 2p spectra are fitted using the S 2p1/2 and S 2p3/2 doublet with a fixed 1:2 peak area ratio and 1.18 eV energy separation [27,28].

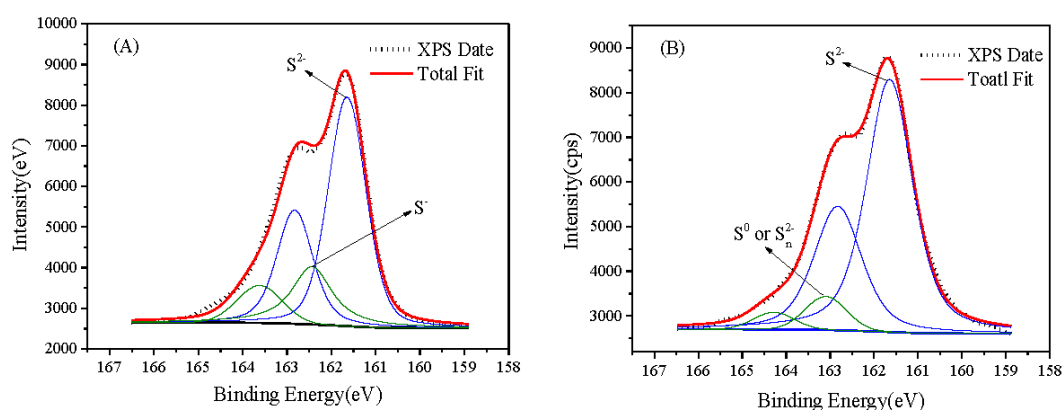
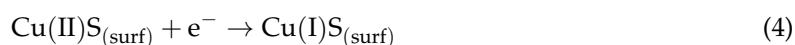
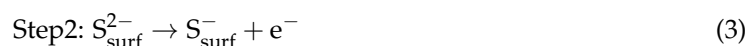
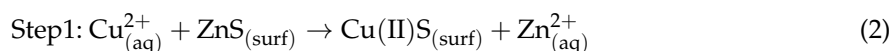


Figure 5. S 2p spectra of sphalerite activated with 2.0×10^{-4} mol/L CuSO_4 at a pH of 7.3 for (A) sphalerite alone, and (B) with pyrite present.

In Figure 5A, a S 2p doublet with S 2p3/2 at a binding energy of 161.6 eV is attributed to S^{2-} from the Zn-S on the sphalerite surface. The peak, with the S 2p3/2 at a binding energy of 162.5 eV, is identified as the S^- from the activation products [6]. However, when sphalerite was activated by CuSO_4 in the presence of pyrite in the pulp, an S 2p peak with S 2p3/2 at binding energy of 163.2 eV was observed as shown in Figure 5B, which represents the S^0 or S_n^{2-} formed on the sphalerite surface [6,29]. This result indicates that the interaction between sphalerite and pyrite in pulp promotes the surface oxidation of S^{2-} on the sphalerite surface, which results in the formation of S^0 or S_n^{2-} on the surface. Rao and Finch [13] suggested that the galvanic interaction between sulfide minerals has an important influence on electrochemical activity of sulfide minerals. The mineral with the higher rest potential acts as the cathode inhibiting the surface oxidation, while the mineral with the lower rest potential will be the anode and promote surface oxidation. In the galvanic contact between sphalerite and pyrite, pyrite will act as the cathode and sphalerite will act as the anode. It is generally well accepted that Cu activation of sphalerite is an electrochemical reaction. The process can be expressed by the following steps:



In Step 2, the Cu^{2+} adsorbed on the sphalerite surface is reduced to Cu^+ , accompanied by the oxidation of S^{2-} to S^- [6,7]. However, the surface oxidation of sphalerite was promoted after galvanic contact with pyrite (Figure 5B). The number of lost electrons numbers will increase due to more S^{2-} being oxidized to S^- , S^0 , or S_n^{2-} on the sphalerite surface. Accordingly, the Cu^+ proportion on the

sphalerite surface increased due to more Cu^{2+} being reduced to Cu^+ by receiving the electrons derived from the oxidation of S^{2-} . In addition, the increased surface oxidation reduces the adsorption of Cu^{2+} on the sphalerite surface, as shown in Figure 2. The species determined on the Cu-activated sphalerite surface—with and without the presence of pyrite—are shown in Table 2.

Table 2. Binding energy (B.E.) and atomic concentration (Atom %) of the elements identified on the Cu-activated sphalerite surface with and without the presence of pyrite in the pulp with 2.0×10^{-4} mol/L CuSO_4 at a pH of 7.3.

Samples	Elements	B.E. (eV)	Species	Atom (%)
ZnS alone	Cu 2p3/2	932.3	Cu(I)	4.58
	Cu 2p3/2	933.4	Cu(II)	1.99
	S 2p3/2	161.6	S^{2-}	18.23
	S 2p3/2	162.5	S^-	2.05
	S 2p1/2	162.8	S^{2-}	9.1
	S 2p1/2	163.7	S^-	1.03
	Zn 2p3/2	1022.09	Zn^{2+}	18.14
	O 1s	532.7	C=O	5.62
	O 1s	533.6	OH $^-$	3.26
	C 1s	284.8	C–C (Ref)	30.55
	C 1s	286.3	O–C–O	3.91
	C 1s	288.2	O–C=O	1.54
	ZnS with the presence of FeS_2	Cu 2p3/2	932.4	Cu(I)
S 2p3/2		161.6	S^{2-}	19.08
S 2p1/2		162.8	S^{2-}	9.54
S 2p3/2		163.2	S_n^{2-} or S^0	1.96
S 2p1/2		164.4	S_n^{2-} or S^0	0.98
Zn 2p3/2		1022.0	Zn^{2+}	17.76
O 1s		532.7	C=O	5.73
O 1s		533.6	OH $^-$	3.51
C 1s		284.8	C–C (Ref)	30.83
C 1s		286.2	O–C–O	4.06
C 1s		288.8	O–C=O	1.4

Results from Table 2 further confirm that the proportion of Cu^+ species upon Cu activation of the sphalerite surface increases after galvanic interaction, but the total atomic concentration of Cu atoms decreases. Therefore, the galvanic interaction between sphalerite and pyrite in pulp will increase the content of Cu^+ species and reduce the adsorption of Cu^{2+} on the sphalerite surface due to increasing the surface oxidation of sphalerite.

3.4. Voltammetry

Linear voltammetry scans were conducted to investigate the difference in the electrochemical characteristics of Cu-activated sphalerite with and without the presence of pyrite in pulp. Each test was conducted with the scan rate of 10 mV/s from 0.0 V to 0.8 V, and the results are shown in Figure 6.

In Figure 6, an anodic current peak was observed at the potential of 0.48 V. Chen and Yoon [5] suggested that the anodic current peak at a potential of around 0.5 V is attributed to the oxidation of activation products Cu(I)–S species on the sphalerite surface. This reaction can be expressed by the following equation:



However, an obvious increase in the oxidation current density was observed when pyrite was present in the pulp during activation, which indicated that the proportion of Cu_2S on the sphalerite surface increased after contact with pyrite. These results are consistent with the results from the XPS

surface analysis. The Cu^+ proportion on activation products increased due the galvanic interaction between sphalerite and pyrite during copper activation.

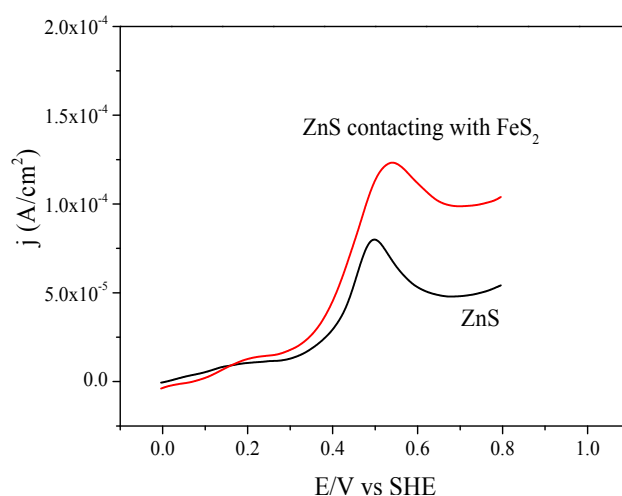


Figure 6. Linear voltammogram of Cu-activated sphalerite with and without the presence of pyrite with 2.0×10^{-4} mol/L CuSO_4 at a pH of 7.3.

4. Conclusions

The effect of the interaction between sphalerite and pyrite on the copper activation of sphalerite was investigated in this paper. By comprehensive comparison of the flotation behavior of sphalerite, adsorption capacity of Cu^{2+} on the sphalerite surface, and XPS and linear voltammogram of Cu-activated sphalerite with and without the presence of pyrite, the following conclusions can be drawn:

- (1) The interaction between sphalerite and pyrite creates competitive adsorption for Cu^{2+} , and also affects the flotation behavior of sphalerite and Cu activation products on the sphalerite surface.
- (2) The flotation recovery and rate of sphalerite decrease with increasing pyrite content in pulp. The adsorption capacity of Cu^{2+} on the sphalerite surface decreases, while the Zn^{2+} released from the sphalerite surface or lattice is reduced due to the interaction between sphalerite and pyrite.
- (3) The interaction between sphalerite and pyrite promotes the surface oxidation of sphalerite, which causes more Cu^{2+} species to be reduced to Cu^+ species on a sphalerite surface. In addition, the oxidation of S^{2-} on a sphalerite surface increases, leading to the presence of S^0 and S_n^{2-} on the sphalerite surface after this interaction.
- (4) The interaction between sphalerite and pyrite has an important effect on the Cu activation of sphalerite, which may be another important factor affecting the selective separation of sphalerite from the associated pyrite.

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