

Research Article

The Adsorption of Cu Species onto Pyrite Surface and Its Effect on Pyrite Flotation

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The adsorption of Cu species onto pyrite surface and its effect on flotation were investigated by using microflotation tests, first-principle calculations, and XPS surface analysis. The results indicated that the flotation of pyrite appears to be activated with CuSO_4 only at alkaline pH, while being depressed at acidic and neutral pH. The adsorption of copper ions on pyrite surface was pH-dependent, and the adsorption magnitude of copper ions at alkaline pH is higher than that at acidic and neutral pH due to a strong interaction between O atom in $\text{Cu}(\text{OH})_2$ and surface Fe atom except for the interaction between Cu atom and surface S atom. At acidic and neutral pH, there is only an interaction between Cu atom and surface S atom. The adsorption was relatively weak, and more copper ions in solution precipitated the collector and depressed the flotation of pyrite. XPS analysis confirmed that more copper ionic species (Cu(I) and Cu(II)) are adsorbed on the pyrite surface at alkaline pH than that at acidic and neutral pH.

1. Introduction

Pyrite is a common sulfide mineral associated with galena, chalcopyrite, and sphalerite. In the selective flotation of Pb-Zn sulfide ores, pyrite is usually depressed at alkaline pH [1–3]. It has been confirmed that pyrite presents poor flotation performance at alkaline pH because of formation of iron hydroxyl on pyrite surfaces [4–6]. CuSO_4 are usually used as an activator for flotation of sulfide mineral [7]. The activation of pyrite is achieved by the formation of CuS-like species on pyrite surface, which improves the surface hydrophobicity of pyrite. Weisener has suggested that activation of pyrite with CuSO_4 follows a single fast step involving Cu(II) adsorption onto the reactive sulfur sites only on the surface with no migration into the bulk pyrite [8, 9].

In some ore-processing plants, the flotation of pyrite is carried out at neutral pH or slight acid conditions, such as Dongguashan copper ores-dressing plant in Anhui, China. Besides, CuSO_4 is often used as an activator for the activation of pyrite [10, 11]. In other cases, due to the association of pyrite with sphalerite in ores, the CuSO_4 used in activation of sphalerite may also influence the flotation of pyrite. However,

unlike sphalerite, pyrite responds well to thiol collector at acidic or neutral pH in the absence of activation. However, the Cu activation of pyrite has been recognized for many years, and many studies focused only on the activation role of CuSO_4 at alkaline pH and considered that pyrite can be activated over the entire pH range [12, 13]. The purpose of this paper is to investigate the different effect of CuSO_4 on pyrite flotation by comparing the adsorption difference of Cu species on pyrite surface at different pH.

2. Experiments

2.1. Minerals and Reagents. The high-purity pyrite crystal samples used in this study were hand-picked and obtained from Yiliang Chihong Mine, Yunnan Province, China. After manual removal of gangue minerals such as quartz and calcite, the samples were dry-ground in a porcelain ball mill and dry-screened to obtain the pyrite particles at 0.075 mm to 0.105 mm. Finally the pyrite samples were packed in jars and sealed under N_2 atmosphere. According to chemical composition analysis, the pyrite samples contained 46.16% Fe, 53.26% S, 0.066% Pb, and 0.21% SiO_2 .

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, HCl, and NaOH of analytical grade from Tianjin number 3 Chemical Reagent Factory were used. Potassium butyl xanthate (K BX) from Sinopharm Chemical Reagent Co., Ltd., was used with 95% purity. Deionized water was used in all of the experiments.

2.2. Flotation. Flotation tests were conducted in Hallimond tube with 1.0 g pyrite sample for each test. The pyrite sample was first mixed with 30 mL of deionized water in a 50 mL beaker. The pH of the slurry was adjusted to the specified pH by using 0.01 mol/L HCl and NaOH solution. Next, CuSO_4 and KBX were added and conditioned for 5 min and 2 min, respectively. Then, the slurry was quickly transferred to the Hallimond tube and floated for 10 min with a N_2 flow rate of $0.01 \text{ dm}^3/\text{min}$. Finally, the floated and nonfloated particles were filtered, dried at 40°C , and weighed for the calculation of recovery. All of tests were repeated three times under the same conditions; the recovery reported in this paper is the average.

2.3. Adsorption Measurement. 1.0 g of pyrite was conditioned with the same condition in the flotation tests. After conditioning, the slurry was filtered through a $0.45 \mu\text{m}$ Millipore filter. The solid sample was used for the adsorption measurement of copper ions and XPS surface analysis, and the filtrate was used for the measurement of KBX concentration.

The amount of copper ions adsorbed onto the pyrite surface was measured by ethylene diamine-tetra acetic acid disodium salt (EDTA) extraction. A 3% solution of AR grade EDTA was prepared and the pH was adjusted to 7.5 by using a 0.01 mol/L NaOH solution. 100 mL of the EDTA solution was placed in a vigorously stirred reaction vessel and continuously purged with N_2 for 10 min to eliminate oxygen from the solution. Then the solid sample was added to the EDTA solution and leached by EDTA for 10 min under continuous N_2 purging. The suspension was then filtered by using a centrifuge at 3000 rpm, the concentration of copper ions in the supernatant was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES), and the solid was dried out and weighed for the adsorption calculation of per unit mass solid. The concentration of KBX in the filtrate was measured by using a UV/Vis spectrometer equipped with a quart cuvette (1.0 mL) as described by Dávila-Pulido et al. [14]. During measurement, deionized water was used as the blank. The absorbance of the solution containing the collector was recorded at a wavelength of 301 nm. The absorbance was converted to concentration according to Beer's law (i.e., adsorption is linearly dependent on concentration). The adsorption amount of collector KBX was calculated by the following equation [15]:

$$\Gamma = \frac{(C_0 - C)V}{1000M}, \quad (1)$$

where Γ represents the adsorption amount (mg/L); C_0 and C represent the initial concentration and the residual concentration after adsorption (mg/L); V are total volume of solution (L) and M the mass of solid sample (g).

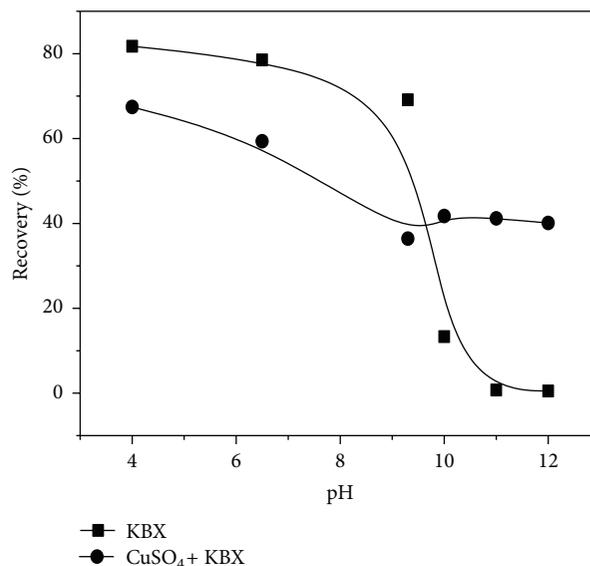


FIGURE 1: Effect of pH on pyrite flotation in the absence and presence of CuSO_4 (conditions: KBX 10 mg/L; CuSO_4 : 10 mg/L).

2.4. XPS Surface Analysis. An X-ray photoelectron spectrometer (XPS, PHI) was used to analyze the surface species present on the pyrite surfaces. A Mg $\text{K}\alpha$ monochromated X-ray source (1253.6 eV) was used in analysis.

2.5. First-Principle Calculation. The adsorption properties of pyrite surface for Cu species were investigated by using first-principle calculations with the CASTEP module (Cambridge Serial Total Energy Package) based on density functional theory. Adsorption studies were performed using 2×2 surface supercell with unit cells. According to the test results, a plane wave cut-off energy of 300 eV and pyrite surface (100) was chosen for all the calculations. A vacuum thickness of 15 \AA was placed between the slabs. The adsorption energy was calculated by the following equation [11, 16]:

$$E_{\text{ads}} = E_{\text{adsorbate}/\text{FeS}_2} - E_{\text{FeS}_2} - E_{\text{adsorbate}}, \quad (2)$$

where E_{ads} represents the adsorption energy (eV), E_{FeS_2} represents the total energy of FeS_2 , $E_{\text{adsorbate}}$ represents the total energy of the adsorbate (eV), and $E_{\text{adsorbate}/\text{FeS}_2}$ represents the total energy of system after adsorption (eV).

3. Results and Discussion

3.1. Effect of pH on Pyrite Flotation in the Absence and Presence of CuSO_4 . Many studies have suggested that as much as 80% to 90% of pyrite (without activation) can be recovered at a pH range of 4 to 6 when using KBX as the collector and the recovery is much lower at other pH values, especially at alkaline pH [7, 10]. The recovery of pyrite as a function of pH in the absence and presence of CuSO_4 is presented in Figure 1.

Figure 1 shows that pyrite exhibits good flotation performance at pH range of 4 to 9 when in the absence of CuSO_4 , and as much as 80% of the pyrite can be floated. But at a pH range of 9 to 12, pyrite is depressed and the recovery decreases

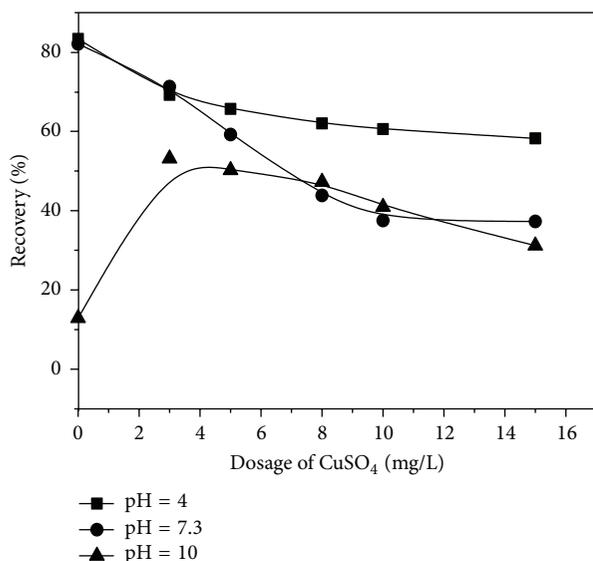


FIGURE 2: Effect of dosage of CuSO_4 on pyrite flotation (conditions: KBX 10 mg/L).

significantly with the increase in pH. The decrease in recovery is attributed to the formation of iron hydroxide on the pyrite surface and the competition between OH^- and collector ions to adsorb on the surface [13]. However, when CuSO_4 is present in the slurry, pyrite recovery has an obvious decrease between pH 4 to 9 and a significant increase between pH 9 and 12. Many previous studies have suggested that copper ions are able to enhance the flotation performance of pyrite and CuSO_4 increases the flotation recovery of pyrite through activation [17, 18]. However, the results from Figure 1 indicate that pyrite is depressed by CuSO_4 at acidic and neutral pH and activated only at alkaline pH, and CuSO_4 plays the role of a depressant at acidic and neutral pH range.

The effect of CuSO_4 dosage on pyrite flotation with different pH is presented in Figure 2.

Figure 2 shows that recovery of pyrite decreases with the increase of CuSO_4 dosage at pH = 4 and 7.3, and the decrease in recovery at pH = 7.3 is greater than that at pH = 4, which may be attributed to the formation of hydrophobic elemental sulphur on the pyrite surface at acidic pH condition. However, a dramatic increase in recovery from 12% to 52% can be observed as the CuSO_4 dosage increases up to 6 mg/L at pH = 10, and the recovery decreases slightly at higher CuSO_4 dosage. Obviously, at acidic and neutral pH, pyrite cannot be activated and is conversely depressed by CuSO_4 , and the activation effect of CuSO_4 on the pyrite flotation is enhanced as the CuSO_4 dosage increases at alkaline pH region.

3.2. Copper Ion and Collector KBX Adsorption. From the above tests and discussion, it can be seen that pyrite is depressed by CuSO_4 at acidic and neutral pH and activated only at alkaline pH. In order to further investigate the effect of CuSO_4 on the flotation of pyrite, the adsorption amounts of copper ions and collector KBX on the pyrite surface as

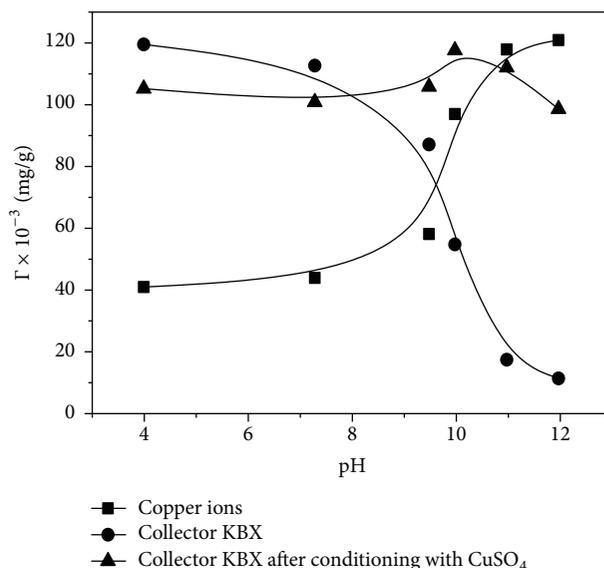


FIGURE 3: The adsorption amount of copper ions and KBX on the surface of pyrite.

a function of pH were studied and the results are shown in Figure 3.

Figure 3 shows that the adsorption of copper ions on pyrite surface increases with the increase of pH, but the adsorption is much lower at pH range of 4 to 9 and increases significantly at pH range of 9 to 12. In addition, the adsorption of collector KBX (without CuSO_4) decreases with the increase of pH and reaches a minimum at pH 12. The trend is consistent with the change in the pyrite recovery without activation. However, when CuSO_4 is present in the slurry, the adsorption amount of collector KBX decreases at pH range of 4 to 8 and has an obvious increase at pH > 8; the increase in adsorption of copper ions causes the Cu activation of pyrite at alkaline pH. Due to the low adsorption of copper ions on pyrite surface at acidic and neutral pH, there is a high concentration of copper ions in solution. These copper ions precipitate with the collector KBX prior to adsorption and reduce the available KBX for flotation, which causes the depression of pyrite.

3.3. First-Principle Calculations. CuSO_4 has different influences on the flotation of pyrite at different pH ranges. These characteristics may be related to both Cu species distribution at different pH and the adsorption properties of pyrite surface for the different Cu species. Therefore, first-principle calculations were used to investigate the adsorption properties of pyrite surface for the different Cu species. The Cu species distribution at different pH range is presented in Figure 4.

Figure 4 shows that the specific copper species presented in solution changes with pH variation of the solution. At pH < 7.5, Cu^{2+} is the primary copper species in solution with a small amount of $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{OH})_2$. At pH range of 9 to 12, the predominant copper species is $\text{Cu}(\text{OH})_2$ with small amounts of $\text{Cu}(\text{OH})^+$, $\text{Cu}(\text{OH})_3^-$, and $\text{Cu}(\text{OH})_4^{2-}$. Obviously, at pH

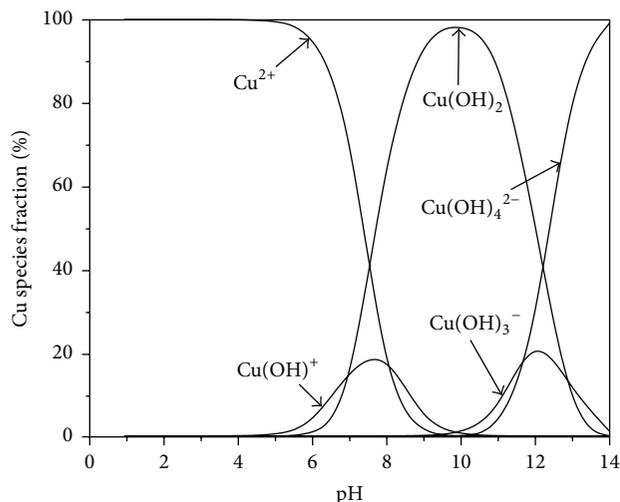


FIGURE 4: Cu species distribution at different pH.

TABLE 1: Adsorption energies of Cu^{2+} and $\text{Cu}(\text{OH})_2$ at different pyrite surface sites.

Adsorbate	Adsorption sites	Adsorption energy (eV)
Cu^{2+}	Top site	-285.22
	Hollow site	-285.76
$\text{Cu}(\text{OH})_2$	Top site	-164.54
	Hollow site	-163.91

range of 4 to 12, Cu^{2+} and $\text{Cu}(\text{OH})_2$ are the two main Cu species in solution. According to Chandra's report, Cu^{2+} and $\text{Cu}(\text{OH})_2$ are the two main Cu species in solution for the activation of sulfide minerals [19], so only Cu^{2+} and $\text{Cu}(\text{OH})_2$ were considered in our calculation.

In addition, Weisener has suggested that since the substitution energy required for Cu to replace surface Fe is positive, the activation of pyrite only involves the adsorption of Cu species on pyrite surface and does not migrate to the bulk, so only the adsorption of Cu^{2+} and $\text{Cu}(\text{OH})_2$ on pyrite surface was considered here [10, 20]. The possible adsorption sites of Cu^{2+} and $\text{Cu}(\text{OH})_2$ were tested to determine the stable adsorption configuration of the molecules adsorbed on pyrite surface.

Figure 5 shows the possible adsorption sites of Cu^{2+} and $\text{Cu}(\text{OH})_2$ on pyrite (100) surface, and the values shown in Figure 5 indicate the atomic distance in angstroms. Table 1 shows the adsorption energy of Cu^{2+} and $\text{Cu}(\text{OH})_2$ on the pyrite (100) surface at different surface sites.

The calculation results shown in Table 1 suggest that the most stable adsorption site for Cu^{2+} on pyrite (100) surface is the hollow site with the adsorption energy of -285.76 eV, and the Cu-S atomic distance of 2.273 Å is shorter than the top site with an atomic distance of 2.298 Å. The adsorption of $\text{Cu}(\text{OH})_2$ on the top site with the adsorption energy of -164.54 eV was more stable than adsorption on the hollow site because the Cu-S atomic distance of 2.239 Å is shorter than the hollow site with a distance of 3.512 Å. In addition,

TABLE 2: Mulliken population of bond formation on Cu^{2+} and $\text{Cu}(\text{OH})_2$ adsorbed surfaces.

Adsorbate	Bond	Population
Cu^{2+}	S-Cu	0.19
	O-Fe	0.29

the adsorption energy of Cu^{2+} is lower than the adsorption energy of $\text{Cu}(\text{OH})_2$, which suggests that Cu^{2+} more easily adsorbs on the pyrite (100) surface than $\text{Cu}(\text{OH})_2$. However, during the adsorption of $\text{Cu}(\text{OH})_2$, the atomic distance between O and surface Fe is 2.100 Å. Combined with the data from Table 2, it can be found that a strong covalent interaction between O and surface Fe could be observed due to an overlap of electron clouds between O atom in $\text{Cu}(\text{OH})_2$ and surface Fe atom in addition to the interaction between Cu and surface S, as shown in Figure 6.

During the adsorption of Cu^{2+} , Cu^{2+} is only able to coordinate with surface S active sites to form a CuS-like surface compound. But at alkaline pH, in addition to the interaction between Cu and surface S, there are strong covalent interactions between the O atom in $\text{Cu}(\text{OH})_2$ and surface Fe, which promotes the stable adsorption of $\text{Cu}(\text{OH})_2$ and increases the amount of Cu^{2+} adsorbed on the pyrite surface. At acidic and neutral pH, however, there may be a high concentration of copper ions in solution due to Cu^{2+} coordinating only with surface S atoms. Copper ions precipitate the collector and reduce the concentration of collector available for pyrite flotation and thus depress the flotation of pyrite. On the other hand, previous studies have suggested that nonactivated pyrite exhibits an excellent flotation performance at acidic and neutral pH, and the adsorption of Cu^{2+} on surface S active sites does not result in the increase of flotation performance of pyrite. When the flotation of pyrite was conducted at mildly acidic and neutral pH with CuSO_4 as activator, pyrite may not be activated effectively by CuSO_4 .

3.4. XPS Analysis. In order to further investigate the surface properties and adsorption characteristics of pyrite conditioned with CuSO_4 at different pH, XPS surface analysis was carried out. Figures 7(a)–7(c) show the full XPS spectra of pyrite conditioned with CuSO_4 at pH = 4, 7.3, and 11, respectively.

Compared with Figures 7(a) and 7(b), a distinct high binding energy Cu2p peak can be found at pH = 10 as shown in Figure 7(c). In addition, semiquantitative analysis of the relative surface atomic concentration indicates that surface copper atomic concentration reaches 1.2% at pH = 10, but the concentration is very low at acidic and neutral pH. These results suggest that the adsorption of copper ions on the pyrite surface is stronger at alkaline pH than at acidic or neutral pH.

Figure 7(d) shows the Cu2p spectra of the pyrite conditioned with CuSO_4 at pH = 10. In the Cu2p spectra, two Cu2p peaks could be found at binding energy 933.60 eV and 952.38 eV, respectively. According to Boulton's results,

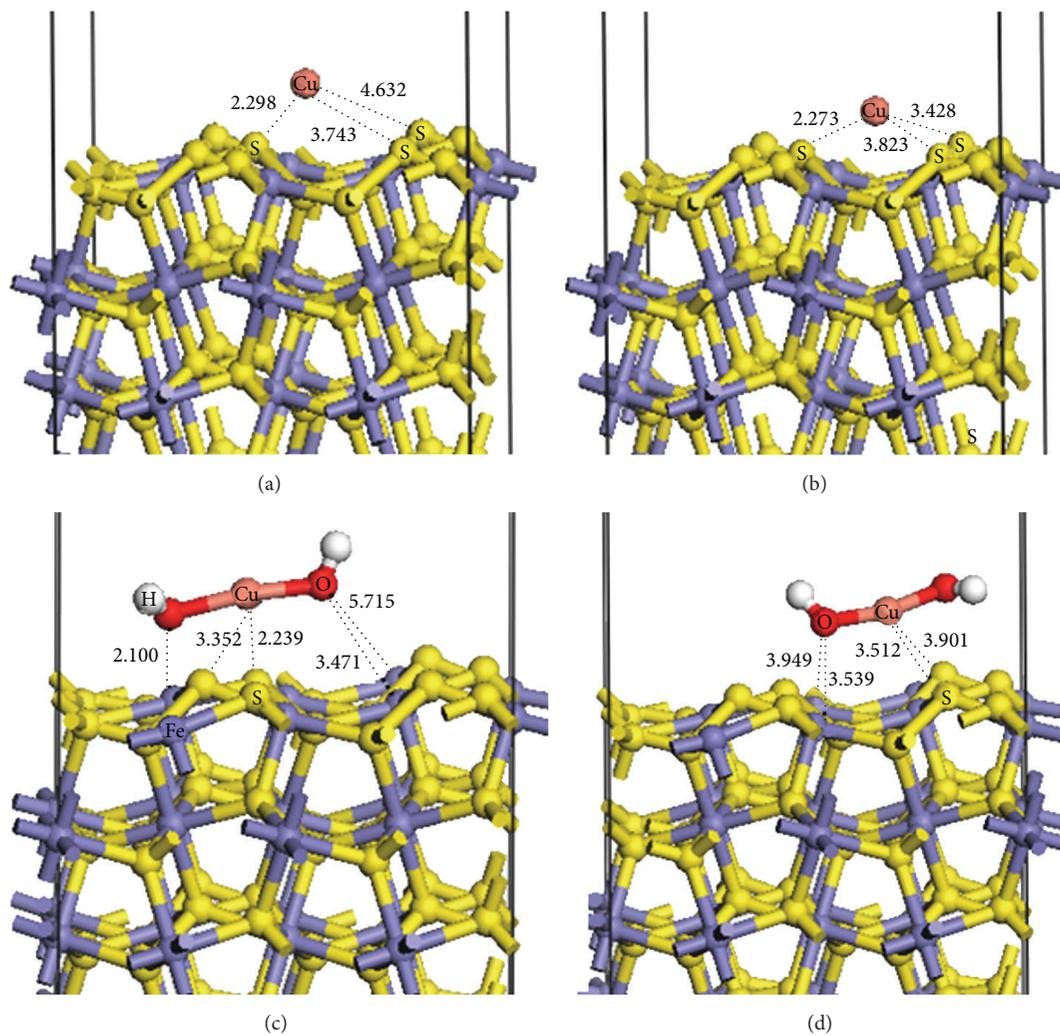


FIGURE 5: The possible adsorption sites of Cu^{2+} and $\text{Cu}(\text{OH})_2$ on the pyrite (100) surface. (a) The adsorption of Cu^{2+} on the top site; (b) the adsorption of Cu^{2+} on the hollow site; (c) the adsorption of $\text{Cu}(\text{OH})_2$ on the top site; (d) the adsorption of $\text{Cu}(\text{OH})_2$ on the hollow site.

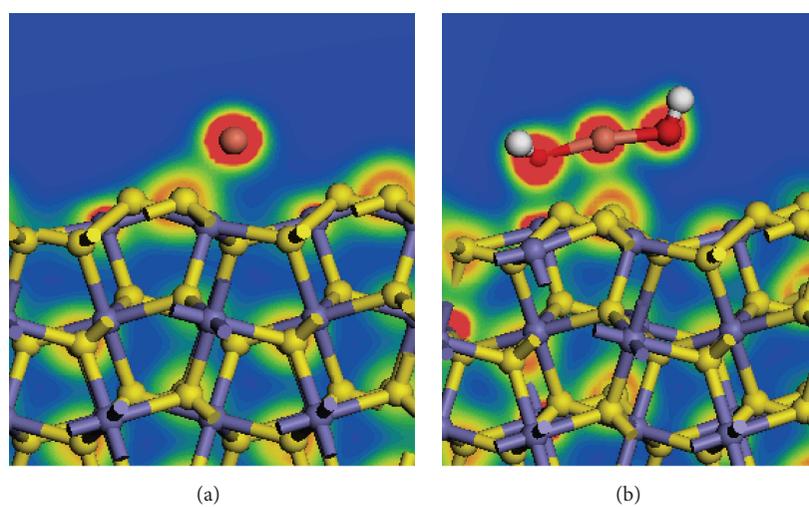


FIGURE 6: Electron density maps after adsorption of (a) Cu^{2+} and (b) $\text{Cu}(\text{OH})_2$.

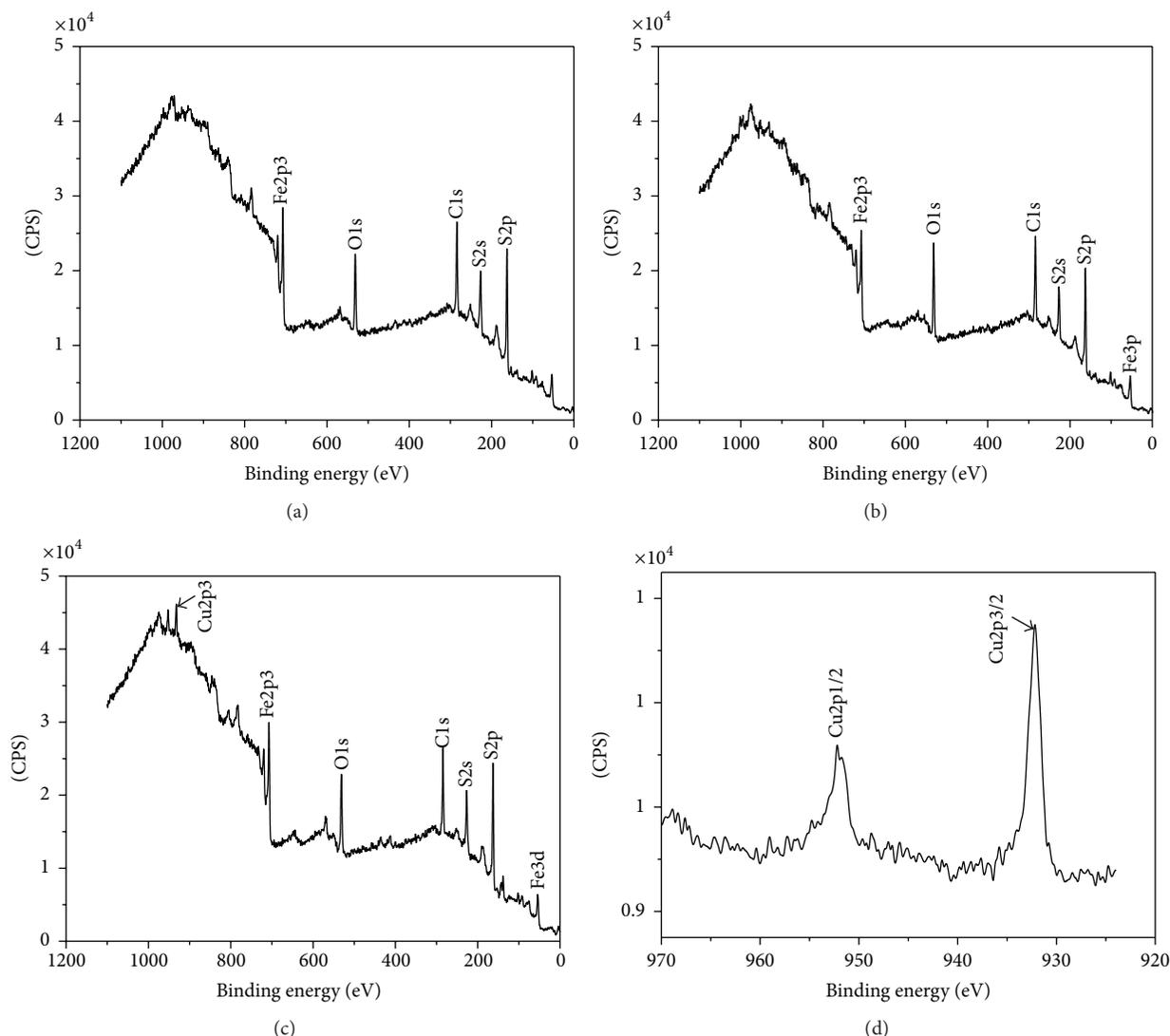


FIGURE 7: XPS spectra of pyrite conditioned with CuSO₄ at different pH. (a) pH = 4, (b) pH = 7.3, and (c) pH = 10. (d) Cu2p spectra of pyrite conditioned with copper sulfate at pH = 10.

the Cu2p_{3/2} peak at binding energy 933.60 eV is attributed to the feature peak of Cu(II), and the Cu2p_{1/2} peak at binding energy 952.38 eV is attributed to the feature peak of Cu(I) [21, 22]. Therefore, we can infer that the surface compounds formed on pyrite surface coexist as Cu(II) and Cu(I) species after Cu adsorption at pH = 10. Weisener and Gerson have suggested that after Cu activation of pyrite, the Cu(I) species on the pyrite surface could be found over the entire pH range, but the Cu(II) species could only be found at alkaline pH ranges due to the coverage by a Cu(II) hydroxyl complex on the pyrite surface at alkaline pH [23]. Additionally, according to studies on the interaction between X⁻ (xanthate ions) and Cu²⁺, the binding energy of Cu²⁺ and X⁻ is larger than that of Cu⁺ and X⁻. The covalent interaction between X⁻ and Cu⁺ is relatively weak, whereas the pyrite activated at alkaline pH is conducive for the adsorption of X⁻ on the pyrite surface [24]. At acidic and neutral pH, the addition of CuSO₄ depresses the flotation of pyrite due to the Cu²⁺

in solution and precipitates the collector. At alkaline pH, the addition of CuSO₄ significantly enhances the floatability of pyrite due to the increase of Cu adsorption on the pyrite surface, which is an important factor affecting the selective separation of sphalerite from pyrite.

4. Conclusions

CuSO₄ has both positive and negative influences on the flotation of pyrite at different pH: the flotation of pyrite is depressed to some extent at acidic and neutral pH and activated at alkaline pH. The adsorption of copper ions on the pyrite surface increases with the increase in pH. Compared with no CuSO₄, the adsorption of collector KBX decreases at acidic and neutral pH while it increases at alkaline pH in the presence of CuSO₄.

First-principle calculations suggest that in addition to the interaction between Cu and surface S atom, a strong

interaction between O atom in $\text{Cu}(\text{OH})_2$ and surface Fe atom can be found during the adsorption of $\text{Cu}(\text{OH})_2$, which results in an increase in the adsorption of $\text{Cu}(\text{OH})_2$ on pyrite surface and thus an increase of Cu adsorption at alkaline pH. Due to the adsorption of Cu^{2+} on only surface S sites at acidic and neutral pH, the amount of Cu^{2+} adsorbed on pyrite surface is lower than $\text{Cu}(\text{OH})_2$, which causes a high Cu^{2+} concentration in solution at acidic and neutral pH, and this Cu^{2+} in solution precipitates the collector KBX and depresses the flotation of pyrite. XPS analysis suggests that a high copper atomic concentration could be found on pyrite surface at alkaline pH. Besides, Cu(II) species coexist with Cu(I) species as the surface compounds formed on the pyrite surface after Cu adsorption at alkaline pH.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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