Density Functional Theory and XPS Studies of the Adsorption of Cyanide on Chalcopyrite Surfaces

Qingmin Nie, Mengyu Wang, Tingsheng Qiu,* and Xianhui Qiu*

ABSTRACT: In this work, both the density functional theory (DFT) calculation and X-ray photoelectron spectroscopy (XPS) were conducted to investigate the depression mechanisms of cyanide on the flotation performance of chalcopyrite. The density functional theory calculation results showed that cyanide could be adsorbed on a chalcopyrite (112) surface spontaneously, which preferably occurred on the surface Fe−Fe hollow site. Both C and N atoms of cyanide could bond with Fe atoms of the chalcopyrite (112) surface, while the interaction of Fe−C bond was more intense, where the Fe 3d orbital donated electrons to the hybrid sp orbital of a C atom forming a back-donating bond. XPS analysis indicated that the chemical interaction between cyanide and surface Fe atoms occurred, resulting in the generation of a hydrophilic iron−cyanide complex on the chalcopyrite surface, which deteriorated the flotation performance of chalcopyrite.

INTRODUCTION

Cyanide leaching is a primary technique for the extraction of precious metals in many gold and silver mines, which offers the benefits of high leaching rates and relatively low costs, 1,2 whereas, it would generate a large number of cyanidation tailings that is generally rich in valuable metal minerals such as chalcopyrite, sphalerite, and galena. With the increasing depletion of mineral resources on a world scale, the recycling of the residual valuable minerals from the tailings has become a necessity.3 Chalcopyrite is a common sulfide mineral in cyanidation tailings, which is one of the major copper-bearing minerals, and a well-developed method for the processing of chalcopyrite by this technique since the cyanide would cause a deleterious effect on the flotation performance of chalcopyrite. However, Bachiller6 thought that the cuprous cyanide complex was the dominant compound that inhibited the floating of chalcopyrite rather than the cupric one due to the higher stability of the cuprous cyanide complex in the slurry. On the other hand, the iron−cyanide complexes were concluded to be the primary compounds that exhibited the depression effects on the flotation performance of this copper sulfide mineral, as reported by Adams.7 Moreover, other researchers8−11 thought that the depression mechanisms of cyanide on the flotation of chalcopyrite were complicated, which depended critically on the flotation pulp environments such as the concentration of cyanide and pulp potential. Though lots of investigations have been conducted, the mechanism by which cyanide depresses the chalcopyrite flotation is not well understood yet.

In recent years, with the rapid development of computer technology and quantum chemistry, the first principles method based on the density functional theory has been widely employed for the study of mineral crystal structures, surface properties, and reagent adsorption, and much research has focused on the first principles study of chalcopyrite. Chen12

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and Edelbro and Edelbro\textsuperscript{13} explored the electronic properties of a chalcopyrite crystal by the mean of the density functional theory and discussed the influences of these properties on the chalcopyrite flotation performance as well as its interaction with flotation reagents. In addition, de Oliveira\textsuperscript{14,15} and Wang\textsuperscript{16} studied the reconstruction of a chalcopyrite surface by density functional theory simulations, and three different reconstruction mechanisms have been proposed for the interpretation of surface passivation in the hydrometallurgical process. The DFT study of the adsorption of water molecules on the chalcopyrite surface was carried out by de Lima,\textsuperscript{17} and the calculation results suggested that the hydrophobicity of the chalcopyrite surface was relatively well. Furthermore, the interactions of flotation reagents such as iodide, iodate,\textsuperscript{18} and 2-mercaptobenzothiazole\textsuperscript{19} with the chalcopyrite surface were extensively investigated by first principles method, which expounded the reaction principles to a certain extent. However, few studies related to the DFT study of the adsorption of cyanide on the chalcopyrite surface have been reported yet.

In this work, the adsorption of cyanide on the chalcopyrite surface was investigated by both density functional theory and X-ray photoelectron spectroscopy, and the reaction principles of cyanide with chalcopyrite were discussed. The research can offer theoretical references for the understanding of cyanide depression mechanism on chalcopyrite as well as the subsequent activation and flotation recovery of chalcopyrite in cyanidation tailings.

\section*{RESULTS AND DISCUSSION}

\textbf{DFT Calculations. Adsorption of CN on the Chalcopyrite (112) Surface.} The (112) surface slab model of chalcopyrite originated from an optimized crystal cell, which experienced the geometry optimization before the adsorption of CN. After surface relaxation, an obvious reconstruction of the chalcopyrite (112) surface took place, forming a hexatomic ring structure composed of Cu, Fe, and S atoms on the first atomic layer of the (112) surface. In this study, the atop, bridge, and hollow sites (Figure 1) were selected as the reactive adsorption sites on the reconstruction (112) surface, and one CN molecule was placed over each adsorption site, respectively, with a distance of 3 Å between the CN molecule and surface atoms for the DFT calculation of cyanide adsorption. Ten adsorption configurations were calculated to simulate the adsorption of CN on the different sites of the chalcopyrite (112) surface, and the adsorption energy of CN on the different sites of the chalcopyrite (112) surface is given in Table 1.

\begin{table}[h]
\centering
\caption{Adsorption Energy of CN on the Different Sites of the Chalcopyrite (112) Surface}
\begin{tabular}{|c|c|}
\hline
adsorption site & adsorption energy (kJ/mol) \\
\hline
atop Cu–C & -246.70 \\
atop Cu–N & -228.56 \\
atop Fe–C & -304.69 \\
atop Fe–N & -281.20 \\
atop S–C & -223.36 \\
Cu–S bridge & -210.67 \\
Fe–S bridge & -288.03 \\
Fe–Fe hollow & -335.90 \\
Cu–Cu hollow & -255.48 \\
Fe–Cu hollow & -293.57 \\
\hline
\end{tabular}
\end{table}

As shown in Table 1, all of the values of the adsorption energy of CN on different sites of the (112) surface were negative, suggesting that the adsorption of CN on the chalcopyrite (112) surface was an exothermic process and CN could interact with the chalcopyrite surface spontaneously. Besides, the adsorption energy was lowest when the CN was adsorbed on the surface Fe–Fe hollow site, which indicated that the preferable adsorption site for CN on the (112) surface was the Fe–Fe hollow site.

The configuration of CN adsorption on the Fe–Fe hollow site of the chalcopyrite (112) surface is shown in Figure 2. It can be seen from Figure 2 that CN was almost parallel to the (112) surface, with the C and N atoms of CN interacting with the Fe atoms on the chalcopyrite (112) surface. The distances between Fe–C and Fe–N were 1.970 and 2.043 Å, which were close to the sum of the covalent radius of Fe–C and Fe–N, respectively, suggesting that the intensive interaction between CN and the chalcopyrite (112) surface occurred and the chemical bonds of Fe–C and Fe–N were formed on the (112) surface after the adsorption of CN. The bond length of Fe–N was longer than that of Fe–C, which indicated that the reaction effect of Fe–C was more intense than that of Fe–N. Accordingly, the adsorption of CN on the Fe–Fe hollow site of the chalcopyrite (112) surface was mainly through the bonding between the C atom of CN and the Fe atom of the chalcopyrite surface.

\textbf{Electronic Structures.} For a detailed interpretation of the mechanism that CN interacts with the chalcopyrite (112)
surface, the electronic properties of the equilibrium adsorption configuration when CN was adsorbed on the Fe-Fe hollow site were studied. Electronic density and electronic density difference maps of CN adsorption on the Fe-Fe hollow site of the chalcopyrite (112) surface are shown in Figure 3a,b, respectively. In Figure 3a, the blue background color represents that the electronic density is zero, while the red and yellow colors indicate the existence of electrons. The obvious overlaps of electron clouds could be found in the areas between CN and surface Fe atoms, showing that the covalent bonds of Fe=C and Fe=N were formed after CN adsorption. The electronic density between Fe and C atoms was greater than that between Fe and N atoms, suggesting that the interaction between C and Fe atoms was stronger than that between N and Fe atoms, which was consistent with the previous analysis. In Figure 3b, the blue area represents losing electrons while the red portion denotes gaining it. It can be seen that the electron transfer from Fe atoms of the mineral surface to C and N atoms of CN took place during the interaction between CN and the chalcopyrite (112) surface.

The density of states (DOS) of CN and the surface Fe atom before and after adsorption are presented in Figures 4 and 5. As shown in Figure 4, the DOS of isolated CN comprised four parts, of which the DOS near $-15.0$ and $-2.9$ eV were the $3\sigma$ and $4\sigma$ orbitals of CN, the DOS near the Fermi level were the full $1\pi$ orbital and semifull $5\sigma$ orbital, and the electronic density near 7.4 eV in the conduction band was the empty $2\pi$ antibonding orbital, which is well consistent with the electronic configuration of cyanide of KK($3\sigma$)$^2$(4$\sigma$)$^2$(1$\pi$)$^4$(5$\sigma$)$^3$(2$\pi$)$^0$. After adsorption, striking changes can be found in the DOS of CN. The entire electronic density shifted to the valence band and the state peak of $5\sigma$ increased apparently, indicating that the CN molecule, especially the $5\sigma$ orbital of CN, obtained electrons. In addition, the nonlocality of $1\pi$ orbital of CN became stronger and two new hybrid peaks emerged at $-4.5$ and $-5.5$ eV, which suggested that the intense interaction between C 2p and Fe 3d orbitals occurred during the CN adsorption. It can be seen from Figure 5 that the DOS of the surface Fe atom changed greatly after the adsorption of CN. The states of the Fe 3d orbital reduced and moved to the conduction band partly, implying that the Fe 3d orbital lost electrons. Furthermore, two new peaks of the Fe 3d orbital could be found near $-4.5$ and $-5.5$ eV, which was attributed to the interaction between the Fe 3d orbital and the CN molecule.

The Mulliken populations of C, N, and Fe atoms before and after CN adsorption are listed in Table 2. The populations of C s and p orbitals increased remarkably, and the electrical charge...
of a C atom shifted from 0.31 to −0.14 after the CN adsorption. As for the N atom of CN, only the p orbital obtained a small number of electrons, leading to a little increase in the negative electrical charges. The populations of Fe s, p, and d orbitals all decreased, and the Mulliken electrons of the Fe d orbital decreased the most. It turned out that the electrons of the Fe d orbital transferred to the CN molecule, especially to the p orbital of the C atom during the interaction. From the molecular orbital theory, there are a semifull 5σ and an empty 2π antibonding orbital in the CN molecule, which results in the electron transfer from the Fe 3d orbital to the sp hybrid orbital of a C atom, forming a back-donating bond after the CN adsorption. Table 3 presents the Mulliken bond populations before and after the CN adsorption. It can be seen that the Mulliken bond population of C−N decreased from 1.59 to 1.57, and the bond length increased from 1.190 to 1.211 Å, which was caused by the existence of the back-donating bond, which could lower the stability of the CN molecule. The populations of Fe−C and Fe−N bonds were 0.48 and 0.22, and the bond length of Fe−C and Fe−N were 1.970 and 2.043 Å, respectively, suggesting that the covalency of Fe−C was stronger than that of Fe−N, and CN was adsorbed on the chalcopyrite (112) surface mainly through the interaction between C and Fe atoms.

**X-ray Photoelectron Spectra Analysis.** Before cyanide treatment, the fresh chalcopyrite sample was analyzed by XPS to determine the surface components, and the full-range XPS spectrum is provided in Figure 6. The C 1s peak in the full-range XPS spectrum of fresh chalcopyrite was attributed to the adventitious carbon, and the O 1s peak might be related to the air contamination or surface oxidation of the mineral samples.

Figure 7 presents the high-resolution XPS spectrum of Cu 2p of a fresh chalcopyrite surface. The Cu 2p XPS spectrum split into 2p1/2 and 2p3/2 peaks. The Cu 2p1/2 peak was centered at 952.3 eV and the Cu 2p3/2 peak was centered at 932.5 eV, which was in agreement with other publications. It has been reported that the existence of cupric species (Cu2+) usually generates a satellite peak around the binding energy of 942 eV. In Figure 7, there was no satellite peak in the Cu 2p spectrum, which indicated that the Cu atoms in chalcopyrite existed in the form of a monovalent state (Cu+). In addition, the Cu LMM peak of fresh chalcopyrite in Figure 8 was centered at 569.1 eV, which was another evidence for the presence of monovalent copper atoms in the chalcopyrite structure.

**Table 3. Mulliken Bond Populations before and after the CN Adsorption**

| bond   | status       | Mulliken bond population | bond length (Å) |
|--------|--------------|--------------------------|-----------------|
| C−N   | before adsorption | 1.59                     | 1.190           |
|        | after adsorption    | 1.57                     | 1.211           |
| Fe−C  | after adsorption    | 0.48                     | 1.970           |
| Fe−N  | after adsorption    | 0.22                     | 2.043           |

Figure 7. High-resolution spectrum of Cu 2p of the fresh chalcopyrite surface.

Figure 8. High-resolution spectrum of Cu LMM of the fresh chalcopyrite surface.

Figure 9 shows the high-resolution XPS spectrum of S 2p of a fresh chalcopyrite surface. The S 2p peaks occurred as doublets of S 2p1/2 and S 2p3/2 with the splitting energy of 1.2 eV. The S 2p spectrum was fitted by four peaks. The peak at 161.4 eV was in accordance with the monosulfide (S^−), the peak at 162.2 eV was due to the disulfide (S_2^2−), the peak at 163.4 eV was related to the polysulfide (S_n^2−), and the peak at 168.5 eV originated from the SO_4^{2−}. These results agreed well with the reported values. It was worth mentioning that the valence states of Fe, Cu, and S atoms in chalcopyrite were +3, +1, and −2, which was in accordance with the DFT calculation results.

To determine the surface species related to the adsorption of cyanide on a chalcopyrite surface, full-range and high-resolution XPS spectra of chalcopyrite were conducted before and after the cyanide adsorption. The full-range XPS spectra of chalcopyrite samples before and after cyanide adsorption are
Figure 9. High-resolution XPS spectrum of S 2p of the fresh chalcopyrite surface.

Figure 10. Full-range XPS spectra of the chalcopyrite before and after cyanide adsorption.

Figure 11. High-resolution spectra of Cu 2p before and after cyanide adsorption.

Figure 12. High-resolution spectra of S 2p before and after cyanide adsorption.

Figure 13. High-resolution spectra of Fe 2p before and after cyanide adsorption.

The N 1s peak was clearly identified from the full-range XPS spectra of the chalcopyrite surface displayed in Figure 10. The N 1s peak was clearly identified from the full-range XPS spectra of the chalcopyrite surface after the cyanide treatment, revealing the presence of cyanide on the mineral surface qualitatively.

The high-resolution XPS spectra of Cu 2p before and after cyanide adsorption are illustrated in Figure 11. The Cu 2p spectrum was deconvoluted into two peaks. The major peak at 932.4 eV was due to FeCuS₂, and the other peak located at 933.3 eV was assigned to CuO, which were consistent with the results of other workers. No obvious shift of the Cu 2p spectrum occurred after the cyanide adsorption, indicating that the Cu species stayed unchanged on the chalcopyrite surface in the process of cyanide treatment. Figure 12 presents the high-resolution XPS spectra of S 2p of chalcopyrite surface before and after treatment in cyanide solutions. It can be seen that there was no change in the S 2p spectrum after cyanide adsorption, which suggested that the chalcopyrite surface was coated with similar S species before and after the cyanide treatment.

The high-resolution XPS spectra of Fe 2p before and after cyanide adsorption are presented in Figure 13. The Fe 2p spectrum of chalcopyrite before the cyanide adsorption was deconvoluted into three peaks. The first peak at 708.1 eV was assigned to FeCuS₂, the second peak at 711.4 eV was due to FeOOH, and the last peak at 713.3 eV was related to Fe₂(SO₄)₃. A new peak at 710.2 eV was detected in the Fe 2p spectrum after the cyanide adsorption, which was close to the binding energy of an iron–cyanide complex ([Fe(CN)₆]³⁻), showing that the cyanide was adsorbed on the chalcopyrite surface chemically, and the iron–cyanide complex was formed after the cyanide adsorption.

Due to the contamination of the chalcopyrite surface by adventitious carbon that can be found on all mineral surfaces,
the majority of C 1s signals on XPS spectra were adventitious hydrocarbon. Accordingly, only the N 1s XPS spectra of the chalcopyrite surface before and after cyanide adsorption were analyzed to discuss the reaction principle between cyanide and chalcopyrite. The high-resolution XPS spectra of N 1s before and after cyanide adsorption are shown in Figure 14. There was no obvious N 1s peak in the high-resolution spectrum of chalcopyrite before the cyanide treatment. However, the N 1s signals can be detected in both full-range and high-resolution spectra of chalcopyrite after the cyanide adsorption. The N 1s spectrum in the high-resolution spectra after cyanide treatment suggested that the chemical interaction between cyanide and surface iron atoms occurred, and the iron–cyanide complex might be the dominant substance that compromised the flotation performance of chalcopyrite.

CONCLUSIONS

In this work, the adsorption of cyanide on the chalcopyrite surface was systematically studied by both density functional theory and XPS, and the reaction principles of cyanide with chalcopyrite were discussed, which can provide the theoretical references for the interpretation of the depression mechanism of cyanide on chalcopyrite. The DFT calculation results revealed that CN could be adsorbed on the chalcopyrite (112) surface spontaneously, which occurred favorably on the Fe–Fe hollow site with an adsorption energy of $-335.90$ kJ/mol. Both C and N atoms of CN bonded with the Fe atoms of the chalcopyrite (112) surface. The interaction of Fe–C was more intense than that of Fe–N, and the Fe 3d orbital donated electrons to the sp hybrid orbital of the C atom, generating a back-donating bond. XPS analysis showed that the chemical interaction between cyanide and surface iron atoms occurred, and an iron–cyanide complex was formed after the cyanide adsorption, which had a detrimental effect on the flotation performance of chalcopyrite.

COMPUTATIONAL AND EXPERIMENTAL DETAILS

Computational Details. All DFT calculations were conducted by the Cambridge Serial Total Energy Package (CASTEP) developed by Payne,26 which is a first principles method based on the density functional theory. Ultrasoft pseudopotential was utilized to describe the interaction between an ionic core and valence electrons, and the valence electron configurations of calculated atoms in this study were $\text{S}3s^23p^4$, $\text{Cu}3d^{10}4s^1$, $\text{Fe}3d^64s^2$, $\text{C}2s^22p^2$, and $\text{N}2s^22p^3$, respectively. The exchange-correlation effect of different electrons was computed by the generalized gradient approximation (GGA) developed by Perdew and Burke,27,28 and an energy cutoff of 360 eV was employed in this simulation. Monkhorst and Pack special $k$-points of a $2 \times 4 \times 1$ grid were adopted for the calculation of the energy and electronic properties of adsorption models. As for the self-consistent electronic minimization, the energy tolerance was $2.0 \times 10^{-6}$ eV/atom, and for the geometry optimization, an energy tolerance of $2.0 \times 10^{-5}$ eV/atom, a maximum displacement of 0.001 Å, and a maximum force threshold of 0.05 eV/Å were adopted. At room temperature, chalcopyrite is an antiferromagnetic material whose Fe atoms in the alternate plane show inverse spin directions along the $c$ axis.29,30 Consequently, different spin directions of Fe atoms at coordinates of $(0, 0, 0.5)$ and $(0, 0, 0.75)$ were set, and the spin-polarization correction was implemented in all of the DFT calculations.

Chalcopyrite crystallizes in the tetragonal system of $I4_2d$ with the lattice parameters of $a = b = 5.289$ Å, $c = 10.423$ Å, and $a = \beta = \gamma = 90^\circ$, and the bond lengths of Fe–S and Cu–S were 2.257 and 2.302 Å.31 The unit cell of chalcopyrite is shown in Figure 15, where the arrows represent the spin directions of Fe atoms. After geometry optimization, the lattice parameters of $a = b = 5.2501$ Å and $c = 10.4103$ Å were obtained, and the valence of Cu, Fe, and S atoms in chalcopyrite were $+1$, $+3$, and $−2$, respectively, which were in good agreement with the experimental values and results of other publications.15,16–18

It was reported19 that only the (112) surface of chalcopyrite showed weak cleavage due to its relatively low surface energy. In addition, Chen32 and Jiao19 reached the conclusion that the (112) surface of chalcopyrite was the predominant cleavage surface because of its geometric and electronic structures. Therefore, the chalcopyrite (112) surface was selected for the DFT calculation of cyanide adsorption in this work.

Figure 14. High-resolution XPS spectra of N 1s before and after cyanide adsorption.

Figure 15. Unit cell of chalcopyrite.
consideration of the influence of slab thickness and numbers of fixed atomic layers on the simulations, convergence tests were carried out, and the stoichiometric chalcopyrite (112) surface slab model with eight layers\(^{14,15,17-19}\) of atoms was employed for the simulation, in which the atop four atomic layers were allowed to relax fully and the last four layers of atoms were fixed in their bulk geometry. Furthermore, for the elimination of the interactions between image slabs, a 15 Å of vacuum layer\(^{18,33,34}\) was placed on the atomic layers along the c-direction, which was adequate for the simulation of the surface properties and cyanide adsorption. The chalcopyrite (112) surface slab model is shown in Figure 16.

\[ E_{\text{ads}} = E_{\text{CN/slab}} - E_{\text{CN}} - E_{\text{slab}} \]  

Figure 16. Chalcopyrite (112) surface slab model.

cyano (CN) was utilized in the DFT calculation for the simulation of the adsorption of anion CN\(^-\) on the chalcopyrite surface, which was employed and proved to be appropriate for the DFT calculation of cyanide adsorption.\(^{34,35}\) The bond length of CN after optimization was 1.190 Å, which was consistent with the result obtained by Chen\(^{34}\) and very close to the experimental value of 1.153 Å, indicating that our calculation outcomes were reliable.

For the calculation of the adsorption energy of CN on the chalcopyrite (112) surface, the following equation was utilized.

The chalcopyrite samples were obtained from Inner Mongolia Province of China, the purity of which was more than 96% indicated by the X-ray diffraction spectrum and chemical assay. Chalcopyrite samples were crushed, ground, and sieved to produce a size fraction of less than 20 \(\mu\)m, which was cleaned by ultrasonic and 1% hydrochloric acid solution and then dried at 40 °C in a vacuum oven. For the preparation of XPS measurement samples, a suspension of 2 g of a chalcopyrite powder sample in 20 mL of 1% sodium cyanide solution was leached for 24 h at a pH 11, while another sample was leached only with deionized water under the identical conditions of leaching time, pulp pH, and a liquid–solid ratio, which was used for the XPS measurement of the chalcopyrite sample before cyanide treatment. Then, the conditioned mineral samples were centrifugated, filtered, and washed with 200 mL of deionized water. After drying in vacuum condition, the chalcopyrite samples were transferred to an X-ray photoelectron spectrometer for measurement.

The ESCALab 250 spectrometer was employed for the XPS measurement, which is equipped with the monochromatic Al Kz as the X-ray source (1486.7 eV), and the vacuum pressure in the measurement chamber was below 2 × 10\(^{-9}\) Pa. The pass energy for full-range scans and high-resolution scans was 100 and 30 eV, respectively. All of the XPS data were analyzed by CasaXPS 2.3.16 software, and the calibration of XPS spectra was performed with the reference energy of 284.8 eV for C 1s.

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**Notes**

The authors declare no competing financial interest.

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