

Article



Cyanide Depression Mechanism for Sphalerite Flotation Separation Based on Density Functional Theory Calculations and Coordination Chemistry

Hang Chen¹, Xiong Tong^{1,2,*}, Xian Xie^{1,2}, Ruiqi Xie¹, Qiang Song¹, Yiqi Cui¹, Youming Xiao¹ and Pulin Dai¹

- School of Land and Resources Engineering, Kunming University of Science and Technology, Kunming 650093, China
- ² Yunnan Engineering Research Center for Metal Tailings Resource Utilization, Kunming 650093, China
- * Correspondence: kgxiongtong@163.com; Tel.: +86-138-8884-1893

Abstract: In this paper, the adsorption of cyanide and its combination with zinc sulfate on the surface of sphalerite (110) was studied by density functional theory (DFT), and its configurational relationship was analyzed by coordination chemistry. The calculation results show that the adsorption configuration stability of CN^- is stronger than that of $Zn(CN)_2$; the chemical bond of $Zn(OH)_2$ is less covalent. The three adsorption modes all make the surface of sphalerite lose more electrons, thereby weakening the reactivity of S and Zn atoms on the sphalerite surface. During the CN^- adsorption process, both the 3d and 4p orbital peak energy levels of Zn decrease, indicating the strong inhibitory effect of CN^- . Coordination chemistry also shows that CN^- matches the Zn ion orbital in sphalerite and the π electron pair on the Zn ion can easily interact with the empty π orbital on CN^- to form π -backbonding.

Keywords: cyanide; sphalerite; DFT; coordination chemistry



Cyanide is an important depressant in the flotation of non-ferrous metal sulfide ores and can effectively inhibit sulfide minerals [1], such as sphalerite, pyrite, and chalcopyrite [2]. Among these minerals, the inhibition effect of cyanide on sphalerite is the most obvious; thus, cyanide has been widely used as a sphalerite depressant [3,4]. Wark et al. found that the formation of $Zn(CN)_2$, a hydrophilic substance, between CN^- and Zn on the surface of sphalerite in pulp can inhibit mineral flotation [5,6]. Seke et al. found that oxidized sphalerite under the xanthate system is in an environment with positive pulp potential, which can be reduced by free CN [7]. Wang and Forssrenr hypothesized that cyanide could react with hydrophobic elemental sulfur and polysulfide to decrease the hydrophobicity of sphalerite [8]. Therefore, cyanide plays an indispensable role in mineral flotation as a sulfide ore depressant. However, researchers have recently developed a new process for inhibiting sphalerite while reducing or replacing cyanide via flotation technology because cyanide is highly toxic and there are strict protection requirements for mining environments [9].

At present, the flotation practice for difficult-to-inhibit sulfide ores shows that the use of cyanide in combination with other depressants can not only strengthen the inhibition, but also reduce the amount of cyanide used. For example, cyanide and zinc sulfate can be mixed and used. In an alkaline environment, $Zn(OH)_2$ and $Zn(CN)_2$ are generated in pulp to form hydrophilic substances, which form an inhibitory effect for sphalerite [10,11]. This process can reduce the amount of cyanide, but there are still environmental problems and risks that endanger human life and safety. Therefore, the development of cyanide-like depressants for sulfide minerals is still an important topic. However, the microscopic mechanism of the interaction of sphalerite with cyanide as depressants remains a "black box", although



Citation: Chen, H.; Tong, X.; Xie, X.; Xie, R.; Song, Q.; Cui, Y.; Xiao, Y.; Dai, P. Cyanide Depression Mechanism for Sphalerite Flotation Separation Based on Density Functional Theory Calculations and Coordination Chemistry. *Minerals* **2022**, *12*, 1271. https://doi.org/10.3390/ min12101271

Academic Editor: Dave Deglon

Received: 20 September 2022 Accepted: 6 October 2022 Published: 8 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). there are different views of their reaction mechanism. Due to its advantages, quantum theory has been increasingly used in recent years to obtain microscopic information related to minerals. Density functional theory (DFT) simulations are effective for simulating the surface microstructure and adsorption mechanisms of minerals, thus enabling the prediction and interpretation of interactions between mineral surfaces and various reagents at the electronic level [12–14]. DFT calculations provide information on the adsorption energies of reagents and atoms present on the mineral surface, enabling the determination of the energy difference [15–17]. At the same time, coordination chemistry is used to describe metal ions and ligands in minerals, which helps to analyze the interaction between flotation reagents and metal ions on the mineral surface [18–21].

In this study, we employed DFT calculations and coordination chemistry to investigate the adsorption mechanism of CN^- on the surface of sphalerite and compared it with $Zn(CN)_2$ and $Zn(OH)_2$. The difference between cyanide and zinc sulfate as depressants is shown, revealing the reason for the strong inhibition of cyanide. This work provides an indepth understanding of the inhibitory mechanism of CN^- on sphalerite from a microscopic perspective, providing new clues for the development of depressants for sulfide ores.

2. Computational Methods

In this paper, the CASTEP module in Material Studio 2019 software was used for all energy optimization and structural calculations. The method applied by the CASTEP module is first principles under the framework of DFT. According to previous calculations, the used calculation is based on the sphalerite structure (ZnS) and its space group is F-43m [16,22]. This calculation adopts the generalized gradient functional to approximate the generalized gradient approximation (GGA) functional, the mitigation correlation energy is described by the (PW91) form gradient correction function proposed by Perdew and Wang, and the interaction between ionic nuclei and valence electrons is described by the ultrasoft pseudopotential. The valence electron configurations of the elements involved in this calculation are H 1s¹, O 2s² 2p⁴, Zn 3d¹⁰4s², S 3s²3p⁴, C 2s²2p² and N 2s²2p³. The energy cutoff value of the valence electron plane wave function was set to 410 eV and all calculations were completed in reciprocal space. The Monkhorst-Pack scheme was adopted for the integral calculation of the total energy and charge density of the system in the Brillouin region, and the k-point set network was set to $2 \times 3 \times 1$. A convergence tolerance of 2.0×10^{-6} eV/atom was employed for self-consistent electronic minimization and an energy tolerance of 2.0×10^{-5} eV/atom, a maximum force tolerance of 0.05 eV/Å, and a maximum displacement tolerance of 0.002 Å were employed for geometry optimization. Considering that sphalerite is a non-magnetic mineral, all atoms are allowed to relax in the calculation process and non-spin results are used to analyze the data, regardless of the influence of spin on calculation results.

Harmer et al. used X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and theoretical methods to measure the surface energy of each surface of sphalerite, finding that the surface of sphalerite (110) is the main cleavage surface and its surface energy is relatively low [22]. Therefore, the cleavage plane of sphalerite (110) was selected for calculation in this study.

Considering that cyanide is mainly adsorbed onto the surface of sphalerite (110), a $2 \times 2 \times 2$ surface set the vacuum layer to 15 Å with a total of four atomic layers and the geometry of this model was optimized. The optimized sphalerite (110) surface model is shown in Figure 1.



Figure 1. Sphalerite (110) surface after geometric optimization ($2 \times 2 \times 2$ supercell model).

Qiu et al. conducted a comparative study on the possible adsorption sites of CN^- in sphalerite (110) and found that the top site was the site with the strongest adsorption capacity [23]. In order to better discuss the results of geometric optimization and carry out the next calculation, the adsorption points used by subsequent ions are all top positions, which are shown in Figure 2.



Figure 2. CN⁻ top-site adsorption on the surface of sphalerite (110).

When zinc sulfate is used in combination with cyanide, cyanide can form a complex with zinc ions. The reaction equation is expressed as Equation (1):

$$Zn^{2+} + 2CN^{-} = Zn(CN)_2$$
(1)

Zinc sulfate can undergo ionization and hydrolysis reactions in aqueous solution by Equations (2) and (3):

$$ZnSO_4 = Zn^{2+} + SO_4^{2-}$$
(2)

And

$$Zn^{2+} + 2H_2O \rightleftharpoons Zn(OH)_2 + 2H^+$$
(3)

Therefore, the main coordination products of zinc sulfate and cyanide are $Zn(CN)_2$ and $Zn(OH)_2$, as shown in Figure 3.



Figure 3. (a) Zn(CN)₂ and (b) Zn(OH)₂ models after geometric optimization.

The CN^- adsorption energy on the surface of sphalerite (110) is shown by Equation (4):

$$\Delta E_{ads} = E_{slab+CN^-}^{tot} - E_{CN^-} - E_{slab}^{tot}$$
(4)

where $E_{slab+CN^{-}}^{tot}$ and E_{slab}^{tot} are the total energy before and after, respectively, the adsorption of CN^{-} by the sphalerite model; $E_{CN^{-}}$ is the total energy of CN^{-} ; and ΔE_{ads} is the adsorption energy of CN on the surface of sphalerite (110).

The adsorption energy equation of $Zn(CN)_2$ and $Zn(OH)_2$ on the surface of sphalerite (110) is given by Equation (5):

$$\Delta E_{ads} = E_{slab+Zn(CN)_2/Zn(OH)_2}^{tot} - E_{Zn(CN)_2/Zn(OH)_2} - E_{slab}^{tot}$$
(5)

where $E_{slab+Zn(CN)_2/Zn(OH)_2}^{tot}$ and E_{slab}^{tot} are the total energy before and after the sphalerite model adsorbs $Zn(CN)_2$ or $Zn(OH)_2$, respectively; $E_{Zn(CN)_2/Zn(OH)_2}$ is the total energy of $Zn(CN)_2$ or $Zn(OH)_2$; and ΔE_{ads} is the adsorption energy of $Zn(CN)_2$ or $Zn(OH)_2$ on the surface of sphalerite (110).

A collection of sphalerite generally first requires the addition of activated ions and then xanthate, but CN⁻, when added, will react with the activated sphalerite ions in advance to prevent sphalerite activation. Therefore, this study only considers the direct action of xanthate on the surface of sphalerite (110) [24]. The optimized butyl xanthate (BX) model is shown in Figure 4, where S1 and S2 represent S atoms with single and double bonds in BX, respectively.



Figure 4. Butyl xanthate (BX) model after geometric optimization.

The adsorption energy equation of BX adsorbed onto the surface of sphalerite (110) is shown by Equation (6):

$$\Delta E_{ads} = E_{slab+BX}^{tot} - E_{BX} - E_{slab}^{tot}$$
(6)

where $E_{slab+BX}^{tot}$ and E_{slab}^{tot} are the total energy before and after the sphalerite model adsorbs BX, respectively, E_{BX} is the total energy of BX, and ΔE_{ads} is the adsorption energy of BX in sphalerite (110).

Adsorption energy indicates the enthalpy change of the reaction between substances. The greater the absolute value of adsorption energy in negative, the easier it is for the adsorption to occur. All quantum mechanical simulation calculations were carried out in vacuum; thus, calculation results are different from the actual production and testing environment. Calculation results are not completely consistent with the actual effect of mineral reagents. Therefore, the calculation results only provide a certain reference for the adsorption of CN^- , $Zn(CN)_2$ and $Zn(OH)_2$ on the surface of sphalerite (110).

3. Results and Discussion

3.1. Adsorption Energy

After DFT geometric optimization, the optimized adsorption configuration of BX, CN^- , $Zn(CN)_2$, and $Zn(OH)_2$ on the surface of sphalerite (110) is shown in Figure 5.



Figure 5. Adsorption models of (**a**) BX, (**b**) CN^- , (**c**) $Zn(CN)_2$, and (**d**) $Zn(OH)_2$ on the surface of sphalerite (110).

Based on the adsorption model structure of BX, CN^- , $Zn(CN)_2$, and $Zn(OH)_2$ acting on the surface of sphalerite (110), the adsorption energy (ΔE_{ads}) is calculated, as shown in Table 1.

Table 1. Adsorption energy of BX, CN^- , $Zn(CN)_2$, and $Zn(OH)_2$ on the surface of sphalerite (1)	10	J).
--	----	---	----

Adsorption Type	Adsorption Energy (kJ/mol)		
BX + ZnS (110)	-66.12		
$CN^{-} + ZnS$ (110)	-233.88		
$Zn(CN)_2 + ZnS(110)$	-99.76		
$Zn(OH)_2 + ZnS$ (110)	-33.42		

It can be seen from Table 1 that the adsorption energies for the three depressant adsorption modes are all negative, indicating that CN^- , $Zn(CN)_2$, and $Zn(OH)_2$ can all be adsorbed onto the surface of sphalerite (110). The adsorption energy of xanthate on the surface of sphalerite (110) is less than that for CN^- and $Zn(CN)_2$ on the surface of sphalerite (110), indicating that CN^- and $Zn(CN)_2$ have stronger adsorption on the surface of sphalerite (110) than xanthate. As can be seen from Figure 5, the distances between the S1 single bond atom and S2 double bond atom of BX and the Zn atom of sphalerite are 2.33 Å and 2.58 Å, respectively, which are less than or equal to the sum of the radii of S and Zn atoms (2.58 Å). The distance between the C atom of CN^- and the Zn atom of sphalerite is 1.74 Å, which is less than the sum of the radii of C and Zn atoms (2.72 Å). The distance between the Zn atom of Zn(CN)₂ and the S atom of sphalerite is 2.37 Å, which is less than the sum of the radii of Zn and S atoms (2.58 Å). These values show that BX, CN^- , and Zn(CN)₂ can be adsorbed onto sphalerite and bond in this process. The adsorption energy

of CN^- on the surface of sphalerite (110) is greater than that of $Zn(CN)_2$, indicating that the chemical adsorption model of CN^- is more prone to occur than that of the $Zn(CN)_2$ model. The distance between the Zn atom of $Zn(OH)_2$ and the S atom of sphalerite is 2.72 Å, which is greater than the sum of the radii of Zn and S atoms (2.58 Å), and no stable chemical bond is formed.

3.2. Mulliken Population Analysis

In order to further analyze the adsorption differences of CN^- , $Zn(CN)_2$, and $Zn(OH)_2$ on the surface of sphalerite (110), the Mulliken population method was used to study the surface of sphalerite (110) [25]. By analyzing the Mulliken charge and bond population, we may quantitatively understand and compare bonding between atoms.

Table 2 shows the sphalerite Mulliken charge distribution of CN^- , $Zn(CN)_2$, and $Zn(OH)_2$ before and after adsorption on the surface of sphalerite (110). When $Zn(CN)_2$ and $Zn(OH)_2$ are adsorbed onto the surface of sphalerite (110), the Mulliken population charge numbers of Zn and S atoms change in a similar way. That is, the 4s orbital of Zn loses a small number of electrons, and the 4p and 3d orbitals have no obvious change. The 3s orbital of S loses a small number of electrons and the 3p orbital gains a small number of electrons. After CN^- is adsorbed onto the surface of sphalerite (110), the 4s and 3d orbitals of Zn lose more electrons. Although the 4p orbital gains more electrons, the total number of electrons of Zn is still decreasing compared to the unadsorbed CN^- . There is no obvious change in the 3s orbital of S and a small number of electrons are lost in the 3p orbital. In general, the surface of sphalerite (110) loses electrons in the three adsorption modes, which reduces the reactivity of Zn and S atoms to a certain extent. The number of electrons lost during the adsorption of CN^- is the largest, while the number of electrons lost in the other two adsorption modes is similar.

Model	Atom	s	р	d	Total	Charge
ZnS	Zn	0.89	0.69	9.98	11.56	0.44
	S	1.86	4.65	0.00	6.51	-0.51
$ZnS + CN^{-}$	Zn	0.75	0.89	9.91	11.54	0.46
	S	1.87	4.58	0.00	6.44	-0.44
$ZnS + Zn(CN)_2$	Zn	0.84	0.68	9.98	11.50	0.50
	S	1.83	4.71	0.00	6.54	-0.54
$ZnS + Zn(OH)_2$	Zn	0.84	0.71	9.97	11.52	0.48
	S	1.85	4.67	0.00	6.51	-0.51

Table 2. Mulliken charge distribution before and after adsorption of CN^- , $Zn(CN)_2$, $Zn(OH)_2$ on the surface of sphalerite (110).

The Mulliken bond population provided in Table 3 was obtained by calculating CN^- , $Zn(CN)_2$, and $Zn(OH)_2$ in sphalerite (110).

Table 3. Mulliken bond population of CN⁻, Zn(CN)₂, and Zn(OH)₂.

Adsorption Mode	Chemical Bond	Population	Bond Length (Å)
$CN^{-} + ZnS$	Zn-C	0.66	1.74
$Zn(CN)_2 + ZnS$	Zn-S	0.42	2.37
$Zn(OH)_2 + ZnS$	Zn-S	0.10	2.72

From Table 3, the Mulliken bond population value in the adsorption of CN^- is larger than that in the adsorption of $Zn(CN)_2$, indicating that the chemical bonds in the adsorption of CN^- have more charge overlap, and the covalent and stability of the bonds are stronger than that of $Zn(CN)_2$ adsorption. The Mulliken bond population value when $Zn(OH)_2$ is adsorbed was the smallest, which indicates that the chemical bonds overlapped less and

the covalent bonds were weak. This is consistent with the conclusions drawn from the adsorption energy discussion.

Based on the comprehensive adsorption energy and Mulliken population analysis, it can be considered that the adsorption tightness of CN^- is stronger than that of $Zn(CN)_2$. The adsorption effect of $Zn(OH)_2$ is the weakest in terms of adsorption energy and population analysis, so the subsequent discussion does not include $Zn(OH)_2$.

3.3. Density of States (DOS) Analysis

Density of states (DOS) is the most important parameter to describe the state of electron motion in solid-state physics. It has been widely used in solid-state physics, surface science, and interface adsorption. In particular, the partial density of states (PDOS) can be used to determine the contribution of each orbital.

In order to clarify the adsorption mechanism of CN^- and Zn (CN) ₂ on sphalerite (110), the adsorption of CN^- and $Zn(CN)_2$ on sphalerite (110) was compared and analyzed using DOS. Figure 6 shows the local DOS before and after the adsorption of CN^- and $Zn(CN)_2$ on the surface of sphalerite (110).



Figure 6. (a) ZnS, (b) ZnS with Zn(CN)₂, and (c) ZnS with NaCN Zn and S atom partial density of state (PDOS).

As shown in Figure 6, the atomic orbitals of sphalerite are mainly composed of S 3s 3p orbitals and Zn 4s 4p 3d orbitals. The main peak of the 3p orbital of sphalerite S decreased from 2.3 to 1.9 eV and shifted from $-1 \sim -2$ eV to $-2 \sim -3$ eV, with a shallow energy level, after Zn(CN)₂ adsorption. This phenomenon shows that Zn(CN)₂ has an inhibitory effect

on sphalerite but the effect is not obvious above the Fermi level. The main peak of the 3d orbital of Zn is split and the peak is reduced to less than 12 eV after the adsorption of CN^- on the surface of sphalerite (110). This indicates that CN^- has a strong inhibitory effect on sphalerite and is higher than that of $Zn(CN)_2$.

3.4. Coordination of CN^- with Zn Ions on the Sphalerite Surface

 CN^- has the ability to interact with Zn ions on the surface of sphalerite in coordination. To determine the reason CN^- has a strong effect as a depressant on the sphalerite surface, the molecular structure and orbital characteristic of CN^- from a coordination chemistry perspective are analyzed based on a newly proposed coordination chemistry theory on flotation [26]. Chen suggested that the coordination effect between reagent and metal ions on mineral surfaces is mainly π -backbonding in the flotation of sulfide minerals [18].

For CN⁻, its lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) distribution were dominated by π and σ orbitals, respectively, as shown in Figure 7.



Figure 7. Energy levels and orbital shapes of CN⁻.

From Figure 7, the LUMO of CN^- is an empty π orbital, so CN^- may accept π electron pairs from the sphalerite surface and form π -backbonding. There are π electron pairs in the e and t₂ orbitons of Zn ions in sphalerite. Therefore, the symmetry of CN^- matches that of the Zn ion orbitals on the surface of sphalerite, allowing π -backbonding to occur in chemisorption. As mentioned above, CN^- is used as a strong depressant in the separation of sphalerite from other minerals due to its special structure and orbital properties.

4. Conclusions

Based on DFT and coordination chemistry, the inhibition mechanism of cyanide and the combination of cyanide and zinc sulfate in flotation separation was studied. The simulation results show that the adsorption energy of CN^- directly adsorbed onto the surface of sphalerite (110) is -233.88 kJ/mol and those of $Zn(CN)_2$ and $Zn(OH)_2$ are -99.76 kJ/mol and -33.42 kJ/mol, respectively. Therefore, both $Zn(CN)_2$ and $Zn(OH)_2$ can be adsorbed onto the surface of sphalerite (110). The results of Mulliken population analysis showed that CN^- and $Zn(CN)_2$ form a stable chemical bond with chemical adsorption modes, among which CN^- was the most covalent. All three modes make the Zn and S on the mineral surface lose electrons, thereby weakening the reactivity of the surface of sphalerite during the flotation process. DOS analysis showed that the main peak energy of

the S orbital of sphalerite decreased to a lower energy level after the adsorption of $Zn(CN)_2$. The main peak of the Zn orbital of sphalerite was split and the peak energy decreased; its inhibitory effect is stronger than that of $Zn(CN)_2$ after the adsorption of CN^- . Coordination chemistry analysis showed that the symmetry of CN^- matches that of the Zn ion orbital in sphalerite, which has multiple pairs of π electrons in the e and t_2 orbitals, and makes it easy to interact with the empty π orbital on CN^- to form a π -backbonding, which provided key information for the development of an efficient depressant of sphalerite based on this mechanism.

Author Contributions: H.C.: Investigation, Software, Formal analysis, Validation, and Writing original draft. X.T.: Writing—review and editing, Funding acquisition. X.X.: Mrthodology, Funding acquisition. R.X.: Writing—review and editing, Conceptualization. Q.S.: Methodology, Funding acquisition. Y.C.: Conceptualization, Methodology. Y.X.: Methodology, Supervision, Validation. P.D.: Methodology. All authors have read and agreed to the published version of the manuscript.

Funding: This research is funded by the National Natural Science Foundation of China (No. 52174252) and the Yunnan Major Scientific and Technological Projects (NO. 202202AG050010).

Acknowledgments: We gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 52174252) and the Yunnan Major Scientific and Technological Projects (NO. 202202AG050010).

Conflicts of Interest: The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

BX: Butyl xanthate; DFT: Density functional theory; DOS: Density of states; GGA: Generalized gradient approximation; HOMO: Highest occupied molecular orbital; LEED: Low energy electron diffraction; LUMO: Lowest unoccupied molecular orbital; PDOS: Partial density of state; XPS: X-ray photoelectron spectroscopy.

References

- 1. Wang, H.; Wen, S.; Han, G.; Xu, L.; Feng, Q. Activation mechanism of lead ions in the flotation of sphalerite depressed with zinc sulfate. *Miner. Eng.* 2020, *146*, 106132. [CrossRef]
- 2. Hu, X.; Huang, H.; Chen, Y.; Mao, J. *Theory and Technology of Flotation*; Central South University of Technology Press: Changsha, China. (In Chinese)
- Botz, M.M.; Mudder, T.I.; Akcil, A.U. Cyanide treatment: Physical, chemical and biological processes. In *Developments in Mineral Processing*; Adams, M.D., Wills, B.A., Eds.; Elsevier: Amsterdam, The Netherlands, 2005; pp. 672–702.
- 4. Reddy, G.S.; Reddy, C.K.; Sekhar, D.M.R.; Ravindranath, K.; Chulet, M.R. Effect of formaldehyde and nickel sulphate solutions on the activation of cyanide-depressed sphalerite. *Miner. Eng.* **1991**, *4*, 151–160. [CrossRef]
- Sutherland, K.L.; Wark, I.W. (Australian Institute of Mining and Metallurgy, Melbourne, Australia). Personal communication, 1955.
- 6. Guo, B.; Peng, Y.; Mai, Y. The effect of zinc cyanide on the flotation of gold from pyritic ore. *Miner. Eng.* **2016**, *85*, 106–111. [CrossRef]
- Seke, M.D.; Pistorius, P.C. Effect of cuprous cyanide, dry and wet milling on the selective flotation of galena and sphalerite. *Miner.* Eng. 2006, 19, 1–11. [CrossRef]
- Wang, X.H.; Forssberg, K.S.E. The solution electrochemistry of sulfide-xanthate-cyanide systems in sulfide mineral flotation. *Miner. Eng.* 1996, 9, 527–546. [CrossRef]
- 9. Guo, B.; Peng, Y.; Espinosa-Gomez, R. Cyanide chemistry and its effect on mineral flotation. *Miner. Eng.* **2014**, 66–68, 25–32. [CrossRef]
- 10. Boulton, A.; Fornasiero, D.; Ralston, J. Depression of iron sulphide flotation in zinc roughers. *Miner. Eng.* **2001**, *14*, 1067–1079. [CrossRef]
- 11. Wang, H.; Wen, S.; Han, G.; Feng, Q. Effect of copper ions on surface properties of ZnSO4-depressed sphalerite and its response to flotation. *Sep. Purif. Technol.* **2019**, *228*, 115756. [CrossRef]
- 12. Chen, Y.; Chen, J.; Guo, J. A DFT study on the effect of lattice impurities on the electronic structures and floatability of sphalerite. *Miner. Eng.* **2010**, *23*, 1120–1130. [CrossRef]
- 13. Chen, J.; Wang, L.; Chen, Y.; Guo, J. A DFT study of the effect of natural impurities on the electronic structure of galena. *Int. J. Miner. Process.* **2011**, *98*, 132–136. [CrossRef]

- 14. de Oliveira, C.; Duarte, H.A. Disulphide and metal sulphide formation on the reconstructed (001) surface of chalcopyrite: A DFT study. *Appl. Surf. Sci.* **2010**, 257, 1319–1324. [CrossRef]
- 15. Sarvaramini, A.; Larachi, F.; Hart, B. Collector attachment to lead-activated sphalerite—Experiments and DFT study on pH and solvent effects. *Appl. Surf. Sci.* 2016, 367, 459–472. [CrossRef]
- Chen, Y.; Chen, J. The first-principle study of the effect of lattice impurity on adsorption of CN on sphalerite surface. *Miner. Eng.* 2010, 23, 676–684. [CrossRef]
- 17. Nie, Q.; Wang, M.; Qiu, T.; Qiu, X. Density Functional Theory and XPS Studies of the Adsorption of Cyanide on Chalcopyrite Surfaces. *ACS Omega* **2020**, *5*, 22778–22785. [CrossRef]
- 18. Chen, J. The interaction of flotation reagents with metal ions in mineral surfaces: A perspective from coordination chemistry. *Miner. Eng.* **2021**, *171*, 107067. [CrossRef]
- 19. Hounfodji, J.W.; Kanhounnon, W.G.; Kpotin, G.; Atohoun, G.S.; Lainé, J.; Foucaud, Y.; Badawi, M. Molecular insights on the adsorption of some pharmaceutical residues from wastewater on kaolinite surfaces. *Chem. Eng. J.* **2021**, 407, 127176. [CrossRef]
- 20. Dai, P.; Chen, H.; Chen, L.; Liu, Y.; Wei, Z. Depression mechanism of peracetic acid for flotation separation of chalcopyrite from arsenopyrite based on coordination chemistry. *Miner. Eng.* **2022**, *186*, 107757. [CrossRef]
- Dai, P.; Wei, Z.; Chen, L.; Liu, Y. Adsorption of butyl xanthate on arsenopyrite (001) and Cu²⁺-activated arsenopyrite (001) surfaces: A DFT study. *Chem. Phys.* 2022, 562, 111668. [CrossRef]
- 22. Harmer, S.L.; Goncharova, L.V.; Kolarova, R. Surface structure of sphalerite studied by medium energy ion scattering and XPS. *Surf. Sci.* 2007, *601*, 352–361. [CrossRef]
- Qiu, T.; He, Y.; Qiu, X.; Yang, X. Density functional theory and experimental studies of Cu²⁺ activation on a cyanide-leached sphalerite surface. *J. Ind. Eng. Chem.* 2017, 45, 307–315. [CrossRef]
- 24. Qiu, T.; Nie, Q.; He, Y.; Yuan, Q. Density functional theory study of cyanide adsorption on the sphalerite (1 1 0) surface. *Appl. Surf. Sci.* 2019, 465, 678–685. [CrossRef]
- Mulliken, R.S. Electronic Population Analysis on LCAO–MO Molecular Wave Functions. I. J. Chem. Phys. 1955, 23, 1833–1840. [CrossRef]
- 26. Chen, J. Coordination Principle of Minerals Flotation; Springer: Berlin/Heidelberg, Germany, 2022.