Electronic Structure and Oxidation Mechanism of Nickel–Copper Converter Matte from First-Principles Calculations

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ABSTRACT: The structural and electronic properties of Cu$_{1.96}$S and Ni$_3$S$_2$ present in nickel–copper converter matte and sulfides such as CuS, Ni$_5$S$_9$, NiS, Ni$_2$S$_2$, and NiS$_2$ likely existing as intermediates in the oxidative leaching of the matte, were investigated using first-principles calculations. Analyses of the total and partial density of states (DOS), with electron density and differential charge density, show that Cu–S and Ni–S bonds are of covalent character, and as the ratio of Ni/Cu to S decreases for the sulfides, Cu/Ni-3d orbital energies shift downward, while S-3p orbital energies shift upward. According to the values of their Cu/Ni-3d band centers, the oxidation activity decreases in the order Cu$_{1.96}$S > Ni$_3$S$_2$ > Ni$_5$S$_9$ > NiS > Ni$_2$S$_2$ > NiS$_2$ > CuS. This oxidation sequence leads to thermodynamically favorable substitution reactions between the nickel sulfides and Cu$^{2+}$ for obtaining more stable CuS, which is the theoretical basis of Sherritt Gordon’s selective leaching process.

1. INTRODUCTION

The nickel–copper converter matte is an intermediate from smelting of sulfide or laterite ores for the recovery of nickel and generally consists of dzharleit (Cu$_{1.96}$S), heazlewoodite (Ni$_3$S$_2$), and some magnetic alloys.1,2 Hydrometallurgical processes for the Ni–Cu matte led to products with high purity, less SO$_2$ emissions during refining, and shorter hold-up time of the main base metals and precious metal byproducts.3 There are a few studies on the mechanism of the selective leaching of nickel–copper converter matte from the perspective of thermodynamics and kinetics.2,4,5 Sherritt Gordon’s leaching system (CuSO$_4$·H$_2$SO$_4$·O$_2$) as one of the selectively oxidative leaching technologies, has been used for the extraction of Ni, Cu, and Co in some metallurgical plants.6–8 The selective leaching for Ni–Cu matte based on the Sherritt Gordon process undergoes two stages.9 Nickel is selectively leached out in the CuSO$_4$·H$_2$SO$_4$·O$_2$ solution in the first stage, while the copper sulfides formed are subsequently dissolved in the H$_2$SO$_4$·O$_2$ solution in the second stage. Therefore, most previous works on the leaching mechanism of Ni–Cu matte demonstrated nickel and copper being leached from the sulfides with decreasing Ni to S and Cu to S ratios, respectively. Price and Davenport10 studied the anodic reactions of Ni$_3$S$_2$, β-NiS, and a commercial nickel matte by the galvanostatic method. The results indicated that nickel sulfides lost nickel ions through a series of phase decomposition: Ni$_3$S$_2$ → Ni$_2$S$_2$ → NiS$_2$ → Ni$^{2+}$ + 2S$^0$. Muir and Ho11 further speculated the reaction path of nickel sulfides by chemical analysis. Grewal et al.12 studied the leaching mechanism of INCO Ltd.’s copper refining electrolysis unit: Cu$_2$S + H$_2$SO$_4$ + 1/2O$_2$ = CuS + CuSO$_4$ + H$_2$O, Cu$_3$S + 1/2CuSO$_4$ + 1/2O$_2$ + H$_2$O = CuS + 1/2H$_2$O + 1/2[2Cu(OH)]$_2$, CuSO$_4$·H$_2$SO$_4$·O$_2$, and CuS + 2O$_2$ = CuSO$_4$. There are some papers13–15 reporting the leaching of chalcocite by a two-step process: Cu$_2$S = CuS + Cu$^{2+}$ + 2e and CuS = Cu$^{2+}$ + S$^0$ + 2e. There are a few research studies comparing the preference of the oxidative dissolution of both nickel and copper from their initial sulfide phases and their various sulfide phases formed during each leaching step of the Sherritt Gordon process because it is difficult to confirm the intermediates experimentally for the mixed sulfide system. However, this information is very important for understanding the leaching mechanism of nickel–copper matte in chemistry. The theoretical calculation here deals with comparison of oxidative activities of nickel and copper sulfides and deduces the performance of nickel and copper sulfides in the whole leaching process.

The oxidative leaching behavior of nickel–copper converter matte depends on its properties, which is mainly determined...
the electronic structures.\textsuperscript{16,17} Investigating the crystal structures and electronic band structures of bulk nickel–copper converter matte and the intermediates of the oxidative leaching is important for understanding the oxidation–reduction reactivity of the chemical elements in the matte and its leaching mechanism. The crystal structures and electronic structures of nickel sulfides were widely investigated by density functional theory (DFT) calculations.\textsuperscript{18–20} During the last 2 decades, the d-band model has been widely used to understand variations in chemisorption energies of various adsorbates on transition-metal surfaces and their sulffides.\textsuperscript{20–22} However, there are few investigations\textsuperscript{23,24} on the relationship between the chemical stability and band-center values for the bulk sulfides. It is probably because the chemical stability is a much more complex property compared with the physical properties for the bulk sulfides. Chen et al.\textsuperscript{18} have explained the oxidation mechanisms for different copper sulfides with the frontier orbital theory. The decrease in oxidizability occurs in the order Cu$_3$S > Cu$_2$FeS$_4$ > CuFeS$_2$ > CuS. Wang et al.\textsuperscript{19} reported the electronic and vibrational properties of Ni$_3$S$_2$, Ni$_5$S$_4$, NiS, and NiS by first principles calculations and found that the nickel d-orbitals shift downward in energy, whereas the sulfur p-orbitals shift upward with increasing sulfur content. Here, the combination of the d/p-center values with the positions of the first high peak in the total DOS was used to compare how easily the outer electrons can be removed from the atoms in the sulfides and then to deduce the oxidation activity sequence among the nickel and copper sulfides.

In this work, the bulk properties of copper and nickel sulfides predominantly existed in the nickel–copper converter matte, and the intermediates of the oxidative leaching process have been investigated by first principles calculations. Besides, d-band center analyses were used to predict the dissolution sequence of the sulfides during the oxidative leaching process for the nickel–copper matte. The computational results can provide detailed information for understanding the nickel selectivity of the oxidative leaching for Sherritt Gordon’s process and shed lights on the conventional process, which is important for developing novel processes to separate Ni and Cu more effectively from the nickel matte.

### 2. METHODS

The calculations were performed using the Cambridge Series Total Energy Package (CASTEP) code\textsuperscript{25} based on the DFT. The Perdew–Wang 1991 (PW91)\textsuperscript{26} associated exchange–correlation functional under generalized gradient approximation\textsuperscript{27} was used to carry out the electronic structure calculations. To model the nickel and copper sulfides, the unit cell (1 × 1 × 1) was applied for the calculation. In order to optimize the lattice constant close to the experimental values, the $k$-point and plane wave truncation energy were tested. A cutoff energy of 520 eV was used for plane wave expansions. The $k$-points meshes within the Monkhorst and Pack\textsuperscript{28} framework were set as $4 \times 4 \times 4, 4 \times 4 \times 2, 5 \times 5 \times 4, 7 \times 1 \times 2, 3 \times 3 \times 8, 4 \times 4 \times 4$, and $4 \times 4 \times 4$ for bulk structures of Cu$_{1.96}$S, CuS, Ni$_3$S$_2$, Ni$_5$S$_4$, NiS, Ni$_3$S$_6$, and NiS$_2$, respectively. The Broyden–Fletcher–Goldfarb–Shanno (BFGS)\textsuperscript{29} minimization algorithm was used to optimize the primitive unit cell. Convergence criteria were set as follows: the force on the atoms within 0.01 eV/Å, the stress on the atoms within 0.02 GPa, the atomic displacement within $5 \times 10^{-4}$ Å, and the energy change per atom within $5 \times 10^{-4}$ eV. The electronic properties of Ni$_3$S$_2$ were calculated previously, and the effect of Hubbard $U$ correction on calculation results of the Ni$_3$S$_2$ system was examined.\textsuperscript{30} It was found that the Hubbard $U$ correction was not needed for obtaining results consistent with the experiments.\textsuperscript{31} Thus, the Hubbard $U$ correction was not included in our calculations on the Ni$_3$S$_2$ system. Regarding the Cu$_3$S$_2$ system, the Hubbard $U$ correction with an effective $U$ value ($U_{\text{eff}} = U - J$) of 12 eV was applied, which has previously been successfully employed to study this system by Deng and Zhao\textsuperscript{32} The other parameters selected for the calculations were the default values corresponding to the selected plane wave cutoff energy and the exchange–correlation functional. All data of the initial crystal structures were obtained from the Inorganic Crystal Structure Database (ICSD).\textsuperscript{33}

The crystal structures of Cu$_{1.96}$S and Ni$_3$S$_2$, which are the sulfides mainly present in the nickel–copper converter matte,\textsuperscript{4} and Ni$_5$S$_4$, NiS, Ni$_3$S$_6$, NiS$_2$, and CuS, which are the intermediates during the oxidative leaching process,\textsuperscript{2} were optimized and compared with their XRD patterns for validating the theoretical results. The charge distribution was obtained by Mulliken charge analysis based on the optimized structure. The density of states (DOS) of the sulfur 3p, nickel 3d, and copper 3d-orbitals were calculated.

### 3. RESULTS AND DISCUSSION

#### 3.1. Bulk Properties of Copper Sulfides

The crystal structure of dharleit (Cu$_{1.96}$S) was optimized by the PW91 method. The calculated lattice constants are shown in Table 1. The calculated data are consistent with the experimental measurements,\textsuperscript{34,35} showing the errors are smaller than 1%. Cu$_{1.96}$S has a cubic structure, shown in Figure 1a, where Cu

| compound   | space group | experimental results | computational results | relative error |
|------------|-------------|----------------------|-----------------------|---------------|
| Cu$_{1.96}$S | $F43m(216)$—cubic | $a = b = c = 5.564$ Å\textsuperscript{34,35} | $a = b = c = 5.611$ Å | 0.05 |
| CuS        | $P6_3/mmc(194)$—hexagonal | $a = b = 3.792$ Å | $a = b = 3.854$ Å | 0.02 |
|            |             | $c = 16.344$ Å\textsuperscript{34,35,60} | $c = 16.250$ Å | 0.06 |

#### 3.2. Adsorbates on Transition-Metal Surfaces

The electronic and vibrational properties of Cu$_{1.96}$S and CuS with experimentally measured XRD results are summarized in Table 1. The crystal structures of Cu$_{1.96}$S and CuS are shown in Figure 1a and 1b, respectively.
atoms are present in two different environments, labeled as CuI and CuII. Four CuI atoms form a regular tetrahedron. The CuII atom occupies 1/4 of the tetrahedral mesh and the center of the cubic structure. All S atoms are in the same environment and occupy the apexes of the cubic structure and the centers of the face.36

Covellite (CuS) has a hexagonal structure as shown in Figure 1b, and Cu atoms are present in two different environments, one in the triangular plane as the CuIS3 unit, the other in the tetrahedron as the CuIIS4 unit. In addition, S atoms are also present in two different environments, where one is connected to CuI atoms to form CuI−SI bonds, and the other is connected to CuII atoms to form CuII−SII bonds. The unit cell constitutes the alternating layers of CuS3 and CuS4 units connected by S−S bonds.37,38 The calculated lattice constants are very close to experimental measurements37,39,40 as shown in Table 1.

The total DOS of Cu1.96S and the partial sulfur 3p and copper 3d orbitals are shown in Figure 2. The DOS of Cu1.96S has no energy band gap, and the high-energy level states of the conduction band (CB) are predominantly composed by S-3p states and some CuI/II-3d states. The initial oxidation stages for solid bulk materials should be related to electrons occupying the states below and near the Fermi energy level (Ef), and those faraway from Ef are hardly to be involved in the oxidation reactions.41 Here, more attention is paid to the band states lower than but near Ef. It is found that there is a big difference in the highest value peak positions between CuI and CuII partial DOS. The highest peak position of CuII partial DOS is −1.375 eV versus Ef, while it is −2.987 eV for CuI partial DOS, indicating the electron density distributions of CuI and CuII are strongly affected by their environments. For the total DOS of Cu1.96S, the peak position nearest to the Ef is located at −1.398 eV, which is very close to the highest peak position (−1.375 eV) of CuII partial DOS. Furthermore, the second highest peak position of the total DOS is at −2.989 eV close to the highest peak position (−2.987 eV) of CuI partial DOS. Meanwhile, the electronic states for the highest peak nearest to the Ef are predominantly contributed by CuI-3d, CuII, and S species to a minor extent. Thus, CuII-3d electrons are more easily available compared with CuI-3d or S-3p electrons in Cu1.96S in the bonding orbitals near Ef. Therefore, CuII species in Cu1.96S should be oxidized more easily compared with Cu I and S atoms when an anodic potential is applied to bulk Cu1.96S. The preferable oxidation reaction can be given by eq 1.

\[ \text{Cu}_1^\text{I} \text{Cu}_1^\text{II} \text{S} - 2e = (\text{Cu}_1^\text{II})^{3+} + \text{Cu}_1^\text{I} \text{S} \] (1)

The bonding between Cu and S atoms within Cu1.96S can be observed clearly in Figure 3, which shows the contour maps of electron density distributions in the (111) plane. The electron density between Cu and S atoms indicates the covalent character of Cu−S bonds. The charge population provides a basis for the quantitative analysis of the interaction between atoms.42 From Figure 3a, it can be seen that the number of charge population between CuI−S is 0.36, which is greater than that between CuII−S (0.11), indicating that CuII−S bonds

Figure 2. DOS analysis for Cu1.96S: (a) the total DOS, (b) S-3p, (c) CuI-3d, and (d) CuII-3d partial DOSs.

Figure 3. Contour maps of (a) electron density distributions and (b) differential charge density of Cu1.96S in the plane (111).
are weaker than Cu$^{\text{I}}$–S bonds. The bond length between the different atoms in copper sulfides was calculated and is shown in Table 2 with data of the average charge population. It was found that the bond of Cu$^{\text{I}}$–S is shorter and stronger than the bond of Cu$^{\text{II}}$–S. Furthermore, Cu$^{\text{II}}$–S bonds are weaker than Cu$^{\text{I}}$–S bonds in terms of their different charge populations because of their different environments. It can be deduced that both Cu$^{\text{I}}$ and Cu$^{\text{II}}$ atoms should be preferably involved in the oxidation reaction when the anodic potential is applied to CuS. The oxidation reaction can be given by eq 2.

$$\text{CuS} + 2e^- = \text{Cu}^{\text{I/II}} + \text{S}^{\text{I/II}}$$

Comparing the DOS of Cu$_{1.96}$S with CuS, the Cu-3d orbitals in CuS shift downward in energy, while S-3p orbitals shift upward. It can be concluded that Cu$^{\text{II}}$ atoms in CuS are more difficult to be oxidized, and the Cu–S bond is of higher covalent character in CuS.

Table 2. Average Charge Population between Two Atoms in Cu$_{1.96}$S and CuS

| compound | bond | charge population | bond length/nm | average charge population per unit bond length/(charge/nm) |
|----------|------|------------------|----------------|----------------------------------------------------------|
| Cu$_{1.96}$S | Cu$^{\text{I}}$–S | 0.36 | 2.409 | 0.1494 |
| Cu$^{\text{II}}$–S | 0.11 | 2.782 | 0.0395 |
| CuS | Cu$^{\text{I}}$–S$^\text{I}$ | 1.34 | 2.303 | 0.5818 |
| Cu$^{\text{II}}$–S$^\text{II}$ | 1.42 | 2.192 | 0.6492 |

Figure 4. DOS analysis for CuS: (a) total DOS, and of (b) S-3p, (c) Cu$^{\text{I}}$-3d, and (d) Cu$^{\text{II}}$-3d partial DOS.

The electron density distributions of CuS in the (111) plane were calculated and are shown in Figure 5, illustrating that more electrons are distributed along the Cu–S bonding direction. The electron density population between Cu$^{\text{I}}$ and S is similar to that between Cu$^{\text{II}}$ and S, which is probably one reason for the similar partial DOS of Cu$^{\text{I}}$ and Cu$^{\text{II}}$. In addition, it can be seen from Table 2 that the Cu$^{\text{I}}$–S$^\text{I}$ bond length and average charge population are similar to the Cu$^{\text{II}}$–S$^\text{II}$ bond, which is consistent with the result of the charge population. The electrons located in the middle of S$^\text{I}$–S$^\text{I}$ bonds indicated that the S–S bonds are covalent. The calculated differential charge density of CuS in the (111) plane is shown in Figure 5b. It was found that Cu$^{\text{II}}$ atoms transfer electrons to S atoms, and electrons aggregate near S atoms. In contrast to Cu$_{1.96}$S, there is almost no interaction among S atoms in CuS, while there is a covalent bonding between S$^\text{I}$–S$^\text{II}$ dimers.
3.2. Bulk Properties of Nickel Sulphides. The crystal structures of Ni₃S₂, Ni₇S₆, NiS, Ni₃S₄, and NiS₂ are shown in Figure 6. Ni₃S₂ is a hexagonal bevel structure in which S atoms form a slightly distorted body-centered cubic array, and Ni atoms occupy a distorted tetrahedral gap. Whereas, NiS has a hexagonal structure, in which three Ni atoms form a triangle, and five S atoms are located at the corner of a square pyramid shown in Figure 6b. As shown in Figure 6c, Ni₇S₆ has five types of Ni atoms and three types of S atoms in an orthorhombic structure. Polydymite Ni₃S₄ has a cubic structure, in which Ni atoms are present in two different environments and S atoms in the same environments, as Ni₃Ni₄S₄ shown in Figure 6d. Pyrite NiS₂ has a cubic structure, as shown in Figure 6e, in which the Ni atoms are located in the face-centered-cubic sublattice. The centers of the sulfur dimers occupy the sites on the midway between the cubic edges and body center. The calculated lattice parameters of Ni₃S₂, Ni₇S₆, NiS, Ni₃S₄, and NiS₂ are very close to the experimental data as shown in Table 3.

The total DOSs of Ni₃S₂, Ni₇S₆, NiS, Ni₃S₄, and NiS₂ are shown in Figure 7. The DOS distributions for all the five nickel sulphides are quite similar to one another. The Ni-3d states below the Fermi level contribute the most to the highest peak and dominant peaks in the total DOS, while S-3p states contribute most to the top of the total DOS. Because the bonding states contain the contribution from Ni-3d and S-3p states, the Ni–S bonds with nickel sulphides should have some covalent character. Comparing the partial DOS of the five nickel sulphides, an important feature is that the Ni-3d orbitals shift downward in energy, while S-3p orbitals shift upward as the ratio of Ni to S decreases. For Ni₇S₆ with the highest ratio of Ni to S, the DOS from −5.0 to 0 eV is mainly contributed by Ni-3d states. Meanwhile, the total DOS in the same region is highly hybridized between Ni-3d and S-3p states for NiS₂, with the lowest ratio of Ni to S, and the p–d hybridization leads to the metallic behavior of NiS₂. It can be deduced that the bonding between Ni and S in NiS₂ is the most covalent.

To explore the bonding information, the contour maps of the electron density distribution and differential charge density of the nickel sulphides are shown in Figure 8, where the projected planes are marked. For all the five sulphides, the electron density around Ni and S ions are approximately spherical, but more electrons accumulate between Ni and S along the bonding directions. It can be deduced that Ni–S bonds are of mixed ionic-covalent nature besides the expected metallic bonding.

3.3. Anodic Dissolution Feasibility of Nickel–Copper Converter Matte. The usual way to extract nickel from sulphide ores consists of concentrating by flotation, smelting concentrates to obtain a nickel matte, grinding and separating copper and nickel sulphides by flotation, casting the high-grade nickel matte to anode, and finally electrolytic refining. Typically, nickel matte contains Ni–Fe alloy, heazlewoodite (Ni₅S₄ 50–65 wt %), and dzharleit (Cu₁.₉₆S₃ 0–45 wt %). The various commercial methods of processing the nickel matte have been developed for many years. For the Sherritt Gordon process, nickel and copper in nickel matte can be selectively dissolved into solution by atmospheric and pressure leaching processes. Muir and Ho found the anodic
dissolution behavior of Ni₃S₂ by the electrochemical methods. They concluded that the reaction pathway is determined by the anodic potential as summarized in eqs 3−6,11 although the actual reactions that occurred are still not fully known.

In order to compare the feasibility and sequence of being oxidized for Ni₃S₂, Ni₇S₆, NiS, Ni₃S₄, and NiS₂, the nickel 3d-band centers and sulfur 3p-band centers were calculated and are shown in Figure 9. It is found that the sulfur 3p-band center is more negative than the nickel-3d band center for each nickel sulfide. It indicates that the nickel atoms should have been more reactive during the oxidation compared with sulfur atoms in the nickel sulfides. This results in the nickel being oxidized in the sulfides, leaving S at the sulfide surface with Ni²⁺ going into solution during the Sherritt Gordon process. Furthermore, it is noted that the nickel 3d-band centers become more negative as the ratio of Ni to S decreases for the five nickel sulfides, which means that the nickel sulfide with the lower ratio should be more difficult to be oxidized. Hence, it can be concluded that the oxidation reactions of the nickel sulfides takes place sequentially while decreasing the ratio of Ni to S, which is in good agreement with the experimental findings in the oxidized leaching of heazlewoodite under acidic conditions.10,11

The calculated values of the Cu 3d-band centers in Cu₁.₉₆S and CuS are shown in Figure 9. Interestingly, the Cu d-band center in Cu₁.₉₆S (−1.37 eV) is the most positive among the

| compound | space group | experimental results | computational results | relative error |
|----------|-------------|----------------------|-----------------------|----------------|
| Ni₃S₂    | R32(155)—trigonal | a = b = 5.745 Å | a = b = 5.738 Å | 0.12 0.28 |
|          |             | c = 7.135 Å        | c = 7.155 Å          |                |
| Ni₇S₆    | Bmmb(63)—orthorhombic | a = 3.274 Å | a = 3.225 Å | 1.41 0.21 |
|          |             | b = 16.157 Å       | b = 16.431 Å         |                |
|          |             | c = 11.359 Å       | c = 11.335 Å         |                |
| NiS      | R3m(160)—trigonal | a = b = 9.619 Å | a = b = 9.588 Å | 0.32 0.01 |
|          |             | c = 3.149 Å        | c = 3.1500 Å         |                |
| Ni₃S₄    |Fd3m(227)—cubic | a = b = c = 9.476 Å | a = b = c = 9.476 Å | 0.04 0.04 |
| NiS₂     | Pa3(205)—cubic | a = b = c = 5.670 Å | a = b = c = 5.628 Å | 0.75 0.75 |

Figure 7. DOS analysis for (a) Ni₃S₂, (b) Ni₇S₆, (c) NiS, (d) Ni₃S₄ and (e) NiS₂. The total and partial DOS of S-3p and Ni-3d orbitals are shown in the top, middle, and bottom figures, respectively.
seven sulfides. It means that copper atoms in Cu$_{1.96}$S should be oxidized most easily among these sulfides. The Cu-3d band center in CuS (−2.40 eV) is the most negative among the sulfides, indicating copper atoms in CuS should be most difficult to oxidize among the sulfides. These results suggest that the presence of Cu$^{2+}$ will help the dissolution of the five nickel sulfides because it is thermodynamically preferable for substitution reactions in obtaining the most stable product of CuS. The S 3p-centers of the two copper sulfides and the five nickel sulfides are lower in energy compared with the Cu/Ni 3d-band of the relating sulfides, which means that all S atoms should have been oxidized later than Cu–Ni atoms in the sulfides.

A simplified illustration diagram of the Sherritt Gordon process is shown in Figure 10. The Sherritt Gordon process can be conveniently divided into three major treatment stages, one atmospheric leach stage and two pressure leach stages. Almost all nickel from the matte can be dissolved into solution
Cu\(^{2+}\) + NiS = CuS + Ni\(^{2+}\)  
(7)

Figure 10. Proposed dissolution process of the nickel matte in the two stages.

by the atmospheric leaching and the first pressure leaching, while copper is dissolved in solution by the second pressure leaching, and iron is removed to the final leach residue. Based on the calculation results here, the oxidation activity decreases in the order Cu\(_{1.96}\)S > Ni\(_{3}\)S\(_{2}\) > Ni\(_{5}\)S\(_{6}\) > NiS > Ni\(_{3}\)S\(_{4}\) > Ni\(_{2}\)S\(_{3}\) > CuS, suggesting that Cu\(_{1.96}\)S should be anodically dissolved first in the atmospheric leaching. Furthermore, Cu\(^{2+}\) ions can be cemented by the displacement reaction with nickel sulfides as shown in eq 7 and trapped within CuS, which is the most stable among the sulfides and can be dissolved in the subsequent pressure leaching process. Because of the much lower oxidation activity of CuS compared with the nickel sulfides, the Sherritt Gordon process is characterized by high selectivity, providing a good metal separation besides efficient metal dissolution. Furthermore, S-3p band centers in the matte sulfides are more negative than Cu-3d band centers and Ni-3d band centers, so elemental sulfur with CuS as the residue is separated from the solution, while nickel sulfides are predominantly oxidized and Ni\(^{2+}\) is moved to solution during the atmospheric leaching step of the Sherritt Gordon process.

\[ \text{Cu}^{2+} + \text{NiS} = \text{CuS} + \text{Ni}^{2+} \]  
(7)

4. CONCLUSIONS

The structural and electronic properties of Cu\(_{1.96}\)S and Ni\(_{3}\)S\(_{2}\) present in nickel—copper converter matte and some other copper and nickel sulfides likely existing as intermediates in the oxidative leaching of the matte are studied by first principles calculations. Analysis of the total DOS and partial DOS, electron density, and differential charge density shows that Cu—S and Ni—S bonds are of covalent character, and Cu/Ni-3d orbital energies decrease, while S-3p orbital energies increase as the ratio of Ni/Cu to S decreases in the order Cu\(_{1.96}\)S, CuS, Ni\(_{3}\)S\(_{2}\), Ni\(_{5}\)S\(_{4}\), NiS, Ni\(_{3}\)S\(_{4}\), and Ni\(_{2}\)S\(_{3}\). Comparison of Cu and Ni-3d band centers for all these sulfides indicates that Cu atoms in Cu\(_{1.96}\)S are the easiest to be oxidized and Cu atoms in CuS are the most difficult to be oxidized, while S atoms are harder to be oxidized than Cu and Ni atoms according to the calculated values of S-3p band centers. It can be concluded that the oxidation activity decreases in the order Cu\(_{1.96}\)S > Ni\(_{3}\)S\(_{2}\) > Ni\(_{5}\)S\(_{6}\) > NiS > Ni\(_{3}\)S\(_{4}\) > Ni\(_{2}\)S\(_{3}\) > CuS. The oxidation sequence for these sulfides results in thermodynamically favorable substitution reactions between the nickel sulfides and Cu\(^{2+}\) for obtaining the most stable product of CuS, which is the basis for Sherritt Gordon’s leaching process.

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Notes
The authors declare no competing financial interest. All data included in this study are available upon request by contact with the corresponding author.

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REFERENCES

(1) Xi, Z.; Wang, Z.; Yan, G.; Guo, H.; Li, X.; Hu, Q.; Peng, W.; Wang, J. Hydrometallurgical production of LiNi0.5Co0.15Al0.3O2 cathode material from high-grade nickel matte. Hydrometallurgy 2019, 186, 30–41.

(2) Selivanov, E. N.; Nechvoglod, O. V.; Udoeva, L. Y.; Lobanov, V. G.; Manyachenkov, S. V. Electrochemical oxidation of nickel-nickel metal-sulfide alloys. Russ. J. Non-Ferrous Metals 2010, 50, 577–581.

(3) Dutrizac, J. J.; Chen, T. A mineralogical study of the phases formed during the CuSO4–H2SO4–O2 leaching of nickel-copper matte. Can. Metall. Q. 1987, 26, 265–276.

(4) Selivanov, E. N.; Nechvoglod, O. V.; Lobanov, V. G. The Effect of the Nickel Sulphide Alloys Structure on Their Electrochemical Oxidation Parameters. IFAC Proc. Vol. 2013, 46, 259–262.

(5) Selivanov, E. N.; Nechvoglod, O. V.; Manyachenkov, S. V.; Sergeev, V. A. Electrochemical oxidation of nickel sulfide metallic alloys. Russ. J. Non-Ferrous Metals 2010, 51, 101–108.

(6) Tan, S.; Shen, Y. Recovery of nickel and cobalt from waste alloys. Eng. Chem. Metall. 2000, 21, 294–297.

(7) Shen, Y.; Yue, W.; Li, W.; Tang, Y. Selective recovery of nickel and cobalt from cobalt-enriched Ni-Cu matte by two-stage countercurrent leaching. Sep. Purif. Technol. 2008, 60, 113–119.

(8) Rademan, J. A. M.; Lorenzen, L.; Van Deventer, J. S. J. The leaching characteristics of Ni-Cu matte in the acid–oxygen pressure leach process at Impala Platinum. Hydrometallurgy 1999, 52, 231–252.

(9) Hofirek, Z.; Kerfoot, D. G. E. The chemistry of the nickel-copper matte leach and its application to process control and optimisation. Hydrometallurgy 1992, 29, 357–381.

(10) Price, D. C.; Davenport, W. G. Anodic reactions of NiS2, β-NiS and nickel matte. J. Appl. Electrochem. 1982, 12, 281–290.

(11) Muir, D. M.; Ho, E. Process review and electrochemistry of nickel sulphides and nickel mattes in acidic sulphate and chloride media. Miner. Process. Extr. Metall. Rev. 2013, 115, 57–65.

(15) Provis, J. L.; Van Deventer, J. S. J.; Rademan, J. A. M.; Lorenzen, L. A kinetic model for the acid-oxygen pressure leaching of Ni–Cu matte. Hydrometallurgy 2003, 70, 83–99.

(16) Chen, J. H.; Wang, J. M.; Long, X. H. First-Principle Theory on Electronic Structure of Copper Sulfides. J. Cent. South Univ. 2011, 42, 3612–3617.

(17) Martin, R. M. Electronic Structure: Basic Theory and Practical Methods; Cambridge University Press: Cambridge, 2004.

(18) Jones, R. O.; Gunnarsson, O. The density functional formalism, its applications and prospects. Rev. Mod. Phys. 1989, 61, 679–746.

(19) Wang, J.-H.; Cheng, Z.; Brédas, J.-J.; Liu, M. Electronic and vibrational properties of nickel sulfides from first principles. J. Chem. Phys. 2007, 127, 214705.

(20) Mavrikakis, M.; Hammer, B.; Norskov, J. K. Effect of strain on the reactivity of metal surfaces. Phys. Rev. Lett. 1988, 61, 2819.

(21) Kitchin, J. R.; Norskov, J. K.; Barrete, M. A. Role of strain and ligand effects in the modification of the electronic and chemical properties of bimetallic surfaces. Phys. Rev. Lett. 2004, 93, 156801.

(22) Kitchin, J. R.; Norskov, J. K.; Barrete, M. A.; Chen, J. G. Modification of the surface electronic and chemical properties of Pt(111) by subsurface 3d transition metals. J. Chem. Phys. 2004, 120, 10240–10246.

(23) Tsai, C.; Chan, K.; Nørskov, J. K.; Abild-Pedersen, F. Understanding the Reactivity of Layered Transition-Metal Sulfides: A Single Electronic Descriptor for Structure and Adsorption. J. Phys. Chem. Lett. 2014, 5, 3884–3889.

(24) Vaughan, D. J.; Tossell, J. A. Electronic structures of sulfide minerals — Theory and experiment. Phys. Chem. Miner. 1983, 9, 253–262.

(25) Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. Iterative minimization techniques forab initio total-energy calculations: molecular dynamics and conjugate gradients. Rev. Mod. Phys. 1992, 64, 1045–1097.

(26) Perdew, J. P.; Wang, Y. Accurate and simple analytic representation of the electron-gas correlation energy. Phys. Rev. B: Condens. Matter Mater. Phys. 1992, 45, 13244.

(27) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B: Condens. Matter Mater. Phys. 1988, 37, 785–789.

(28) Monkhorst, H. J.; Pack, D. J. Special points for Brillouin-zone integrations. Phys. Rev. B: Solid State 1976, 13, 5188–5192.

(29) Pirommer, B. G.; Côté, M.; Louie, S. G.; Cohen, M. L. Relaxation of crystals with the quasi-Newton method. J. Comput. Phys. 1997, 131, 233–240.

(30) Zhang, W.-B.; Li, J.; Liu, X.-H.; Tang, B.-Y. Electronic structure and thermodynamic properties of millerite NiS from first principles: Complex fermi surface and large thermal expansion coefficient. Comput. Mater. Sci. 2014, 83, 412–417.

(31) Aycöl, M.; Wolkow, C. Local environment dependent GGA +U method for accurate thermochemistry of transition metal compounds. Phys. Rev. B: Condens. Matter Mater. Phys. 2014, 90, 115105.

(32) Deng, J.; Zhao, Z.-Y. Effects of non-stoichiometry on electronic structure of Cu2S compounds studied by first-principle calculations. Mater. Res. Express 2019, 6, 105513.

(33) Belsky, A.; Hellenbrandt, M.; Karen, V. L.; Luksch, P. New developments in the Inorganic Crystal Structure Database (ICSD): accessibility in support of materials research and design. Acta Crystallogr., Sect. B: Struct. Sci. 2002, 58, 364–369.

(34) Cook, W. R., Jr.; Shiozawa, L.; Augustine, F. Relationship of copper sulfide and cadmium sulfide phases. J. Appl. Phys. 1970, 41, 3058–3063.

(35) Arslan, H.; Flörke, U.; Küçüç, N.; Emen, M. F. Crystal structure and thermal behaviour of copper (II) and zinc (II) complexes with N-pyrrolidine-N’-(2-chloro-benzoyl) thiourea. J. Coord. Chem. 2006, 59, 223–228.

(36) Zhang, Y.; Wang, Y.; Xi, L.; Qiu, R.; Shi, X.; Zhang, P.; Zhang, W. Crystal and Electronic structure of antifluorite Cu2S solar cell absorbers. J. Chem. Phys. 2014, 140, 074702.

(37) Evans, H.; Konnert, J. Crystal structure refinement of covellite. Am. Mineral. 1976, 61, 996–1000.

(38) Morales-García, A.; Soares, A. L.; Dos Santos, E. C.; de Abreu, H. A.; Duarte, H. A. First-principles calculations and electron density topological analysis of covellite (CuS). J. Phys. Chem. A 2014, 118, 5823–5831.

(39) Li, F.; Wu, J.; Qin, Q.; Li, Z.; Huang, X. Controllable synthesis, optical and photocatalytic properties of CuS nanomaterials with hierarchical structures. Adv. Powder Technol. 2010, 198, 267–274.

(40) Isac, L. A.; Duta, A.; Kriza, A.; Emen, M. F. Crystal structure and thermal behaviour of copper (II) and zinc (II) complexes with N-pyrrolidine-N’-(2-chloro-benzoyl) thiourea. J. Coord. Chem. 2006, 59, 223–228.

(41) Lara, R. H.; Vazquez-Arenas, J.; Ramos-Sanchez, G.; Galvan, M.; Lartundo-Rojas, L. Experimental and Theoretical Analysis Accounting for Differences of Pyrite and Chalcopryte Oxidative Behaviors for Prospective Environmental and Bioleaching Applications. J. Phys. Chem. C 2015, 119, 18364–18379.

(42) Marenich, A. V.; Jerome, S. V.; Cramer, C. J.; Truhlar, D. G. Charge Model S: An Extension of Hirshfeld Population Analysis for
the Accurate Description of Molecular Interactions in Gaseous and Condensed Phases. J. Chem. Theory Comput. 2012, 8, S27–S41.
(43) Parise, J. B. Structure of hazelwoodite (Ni$_3$S$_2$). Acta Crystallogr., Sect. B: Struct. Sci. 1980, 36, 1179–1180.
(44) Fleet, M. The crystal structure of heazlewoodite, and metallic bonds in sulfide minerals. Am. Mineral. 1977, 62, 341–345.
(45) Vershinin, A. D.; Selivanov, E. N.; Gulyaeva, R. I.; Sel'menskikh, N. I. Thermal Expansion of Ni3S2 in Ni3S2-Ni Alloys. Inorg. Mater. 2005, 41, 882–887.
(46) Seim, H.; Fjellvåg, H.; Grønvold, F.; Stølen, S. Metastable nickel sulfides with composition close to Ni$_3$S$_6$—stability and structural properties. J. Solid State Chem. 1996, 121, 400–407.
(47) Sowa, H.; Ahsbahs, H.; Schmitz, W. X-ray diffraction studies of millerite NiS under non-ambient conditions. Phys. Chem. Miner. 2004, 31, 321–327.
(48) Rajamani, V. T.; Prewitt, C. The crystal structure of millerite. Can. Miner. 1974, 12, 253–257.
(49) Berry, L. G.; Thompson, R. M. X-ray powder data for ore minerals: The peacock atlas. Mem.—Geol. Soc. Am. 1962, 85, 1–261.
(50) Nowack, E.; Schwarzenbach, D.; Hahn, T. Charge densities in CoS$_2$ and NiS$_2$ (pyrite structure). Acta Crystallogr., Sect. B: Struct. Sci. 1991, 47, 650–659.