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Performance Analysis of Thiocarbonohydrazide as a Novel Selective Depressant for Chalcopyrite in Molybdenite-Chalcopyrite Separation

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Abstract: A novel surfactant, thiocarbonohydrazide (TCH), was synthesized and tested for the first time as a selective chalcopyrite depressant in Cu-Mo separation. Its adsorption mechanisms on chalcopyrite were studied by flotation tests, zeta potential, FTIR, XPS and ToF-SIMS measurements. FTIR and zeta potential analyses suggested that there was a strong chemisorption reaction between TCH and chalcopyrite, resulting in the formation of TCH–copper complexes. XPS and ToF-SIMS measurements further confirmed the chemisorption of TCH onto the chalcopyrite surface and showed that this chemisorption reaction is due to its S and N atoms, which form five-membered chelating rings by releasing H ions.

Keywords: chalcopyrite; molybdenite; separation; thiocarbonohydrazide

1. Introduction

Molybdenite (MoS_2) and chalcopyrite ($CuFeS_2$) are known molybdenum and copper-bearing sulphide minerals [1], and have almost similar natural floatability in the context of mineral processing. For this reason, the separation of molybdenite from chalcopyrite has always been a challenging task, and efforts are now being carried out to synthesize selective reagents that can depress chalcopyrite efficiently during flotation of molybdenite [2]. In most cases, where the molybdenite is only an economical mineral, depressants are usually required to depress the floatability of chalcopyrite and other sulphide minerals. For example, the floatability of chalcopyrite can be minimized with traditional inorganic depressants including cyanide, sodium sulphide and Nokes' reagent, as well as many other depressants [3]. These inorganic depressants are very toxic and hazardous to health and plants, and the higher dosages required result in high cost and low selectivity [4]. Needless to say, with increasingly strict demands in terms of both environmental and safety regulations, it is imperative to replace these highly toxic and poorly selective depressants with more environmentally friendly and more highly selective reagents in industrial practices [5]. Studies have suggested that if molybdenite is present with economical amounts of copper ores, the molybdenite is first floated along with other floatable minerals, and then subsequently selectively refloated or depressed to receive the separated copper and molybdenum products [1,6]. Hydrophilic polymers, including dextrin, starch glue, dyes, lignosulfonates, humic acids, polyacrylamides, and degradation products of polyacrylamide, are typically used as molybdenite depressants [6–9]. Although considerable work has been done on the use of macro-organic compounds as molybdenite depressants, to our knowledge there have only rarely been reports on the application of these compounds in the flotation separation of Cu-Mo minerals in industrial practices. The approach whereby molybdenite, rather than chalcopyrite, is floated is mainly due to the mass balance consideration of different metals. There are reports in the literature that the content of molybdenite in Cu-Mo bulk concentrate is usually much lower than that of chalcopyrite; hence, the depression of molybdenite during flotation of chalcopyrite would certainly lead to the mechanical entrainment of molybdenite [1,10]. Compared with inorganic and macro-molecular depressants, micro-molecular organic depressants have advantages of cost efficiency, ready availability, better selectivity and environmental friendliness [11]; most importantly, they can be designed and synthesized according to practical applications [12]. Over the past few years, 2,3-disulfanylbutanedioic acid (DMSA) [4], disodium carboxymethyltrithiocarbonate (DCMT) [13], disodium bis(carboxymethyl)-trithio carbonate (DBT) [14], acetic acid-[(hydrazinylthioxomethyl) thiol]-sodium(AHS) and 4-amino-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one(ATDT) have been used as chalcopyrite depressants in the selective flotation of molybdenite [2,10]. Additionally, sodium 2,3-dihydroxypropyl dithiocarbonate (SGX), O,O-bis(2,3-dihydroxypropyl) dithiophosphate(DHDTP) and acetic acid-[(hydrazinylthioxomethyl)-thiol]-sodium (AHS) have shown good selective depression of galena [15–17]. Although extensive work has been done on the development of micro- and macro-molecular depressants for copper-molybdenum flotation separation, only sodium thioglycollate and pseudo glycolythiourea acid have been used as depressants in the selective depression of chalcopyrite in industrial practices in China [18]. Therefore, the development of novel organic compounds with the advantages of low cost, better selectivity, good stability and environmental friendliness for Cu-Mo flotation separation is still a challenging task that will attract much attention in the future.

Nowadays, the derivatives of hydrazine are receiving much attention because of their flexibility and versatility in the synthesis of many other functional organic compounds. It has been found that organic thio derivatives of thiosemicarbazide, thiosemicarbazones, hydrazine, thiohydrazide, thiocarbohydrozones and thiohydrazones dominate a large proportion of the fields of organic, metal-organic frameworks and coordination chemistry [19–21]. Potential compounds that contain N, O and S donor atoms with different coordination modes provide flexibility to the ligands, which can then coordinate with transition metal ions in a neutral or deprotonated form, thus yielding mono- or poly-nuclear complexes [22,23]. Recently, transition metal complexes taking the hydrazine moiety have drawn considerable attention because of their structural diversity, variable binding modes and promising biological implications due to the presence of chelatophore group of donor atoms in the coordination sphere [24,25]. It has been reported that molecules that possess an S–C–N–N linkage show a powerful attraction to some metal ions and could potentially bind to a metal ion in a bidenate fashion through the S atom and the second N atom [23]. There is a series of compounds, such as thiosemicarbazones, that contain the structural unit S–C–N–N, which allows for bidenate coordination with metal ions through S and N atoms to make a stable five-member ring by releasing H ions into aqueous solutions [26–28]. Such a dominant attraction of sulphur and nitrogen atoms to transition metal ions offers potential applications of hydrazine derivatives for the modification of ore surface and subsequent flotation response of sulphide ores, such as chalcopyrite and galena [2]. Encouraged by these observations, we hoped to synthesize some micro-molecular compounds (with the donor atoms of N and S), with a view to exploring their potency as chalcopyrite depressants. In the development of such new bidenate chalcopyrite depressants, detailed research of their structures and adsorption modes is imperative.

In our previous studies, it was shown that acetic acid-[(hydrazinylthioxomethyl) thiol]-sodium and 4-amino-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one adsorbed onto chalcopyrite surfaces and changed their surfaces from hydrophobic to hydrophilic [2,10]. Interestingly, these compounds could be applied as potential depressants for chalcopyrite in bench-scale Cu-Mo flotation separation. In the continuation of our project to develop novel reagents with good selectivity, the present investigation deals with the synthesis of thiocarbonohydrazide as a new alternative chalcopyrite depressant for Cu-Mo flotation separation. The depression mechanism of thiocarbonohydrazide to chalcopyrite was evaluated and confirmed by zeta potential, Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS) and Time of Flight-Secondary Ion Mass Spectrometry (ToF-SIMS).

2. Materials and Methods

2.1. Reagents and Mineral Samples

Thiocarbonohydrazide, the dominant reagent used in the present investigation, was prepared by reacting carbon disulphide with hydrazine [29], and its molecular structure is given in Figure 1. After crystallization from distilled water, its purity was determined to be higher than 98%. Other reagents were purchased from a local supplier. Except for batch scale tests, distilled water was used throughout the experimental work. Representative samples of chalcopyrite and Molybdenite were collected from Dexin copper mine (Shangrao, China) and China Molybdenum Co., Ltd., (Luoyang, China), respectively. The results of XRD spectra of chalcopyrite and molybdenite indicated that both minerals were 90% pure and met the requirement of the present investigation [10]. A bulk concentrate containing 0.28% Cu and 1.05% Mo, which was obtained from the day shift of Yichun Luming Mining Co., Ltd., was used for the Cu-Mo flotation separation in the batch flotation tests [10].

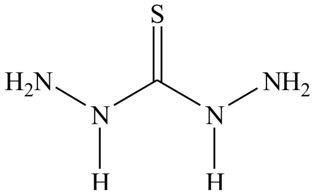


Figure 1. Molecular structure of thiocarbonohydrazide.

2.2. Flotation Experiments

Single-mineral micro-flotation tests were carried out in an XFG-type flotation machine with a capacity of 40 mL. Before the tests, the mineral samples were cleaned with supersonic waves for 5 min, and 2.0 g of the material was used in each test. The samples were conditioned with thiocarbonohydrazide for 5 min, and then the collector (kerosene) and frother (MIBC) were respectively added to the flotation cell with 2 min conditioning time. Froth product was collected after 5 min. The concentrates and tailings were collected, filtered, and dried and weighed for recovery calculations and grade analysis.

Bench-scale flotation separation experiments were carried out in an XFG flotation cell with a volume capacity of 1.5 L (XFG, Jilin Prospecting Machinery Factory, Changchun, China). In the flotation cell, the feed sample was added with recycled water to attain pulp with the required density. The process flowsheet for the bench-scale flotation is shown elsewhere [2]. Froth and tailings were collected, filtered, dried and weighed for the recovery and grade analysis of copper and molybdenum.

2.3. Zeta Potential Measurements

A Malvern Zeta Sizer Nano Series was used to measure the zeta potential of mineral samples. For this, 0.2 g mineral sample (100% passing 5 μm) and 80 mL 0.01 M KNO_3 solutions were mixed in a 100 mL beaker and conditioned for 5 min. During this, pH was adjusted with either HCl or NaOH dilute solutions, followed by 2 min of conditioning after adding appropriate flotation reagents. After another 5 min for sedimentation, the supernatant was moved to a standard cuvette for the zeta potential measurements.

2.4. FT-IR Spectra Measurements

The infrared spectra of thiocarbonohydrazide, thiocarbonohydrazide–Cu^{2+} precipitations, and chalcopyrite before and after treatment with thiocarbonohydrazide were recorded using an IRAffinity-1 spectrometer operating in the range 400–4000 cm^{-1}. In a typical measurement, 1 mg of the mineral sample powders treated or untreated with depressant were weighed out and thoroughly mixed with 100 mg of spectroscopic-grade KBr and placed into pellets to record the spectra.

2.5. X-ray Photoelectron Spectroscopy Measurements

XPS spectra of thiocarbonohydrazide, mineral samples (before and after treatment) and thiocarbonohydrazide–Cu^{2+} precipitations were recorded with a K-Alpha 1063 (Thermo Scientific Co., Waltham, MA, USA) spectrometer with an Al Kα sputtering-ray source operated at 12 kV and 6 mA. The pressure in the analysis chamber was higher than 1.0×10^{-12} Pa during spectral acquisition. Each spectrum was calibrated with respect to a C 1s value of 284.8 eV. XPS Peak 4.1 software was used to fit the XPS peaks.

2.6. Time of Flight-Secondary Ion Mass Spectrometry

An ION-TOF IV instrument (Model 2100 Trift II, Physical Electronics, Lake Drive East Chanhassen, MN, USA) equipped with a Bi primary ion source was used for ToF-SIMS experiments. The treated mineral sample was mounted on indium foil, and the pressure in the analysis chamber was higher than 4×10^{-7} Pa during spectral acquisition. The primary ion beam and acceleration voltage were 15 keV and 5 keV, respectively. The positive and negative spectra were calibrated to $^{63}Cu^+$, $^{65}Cu^+$, $CH_3{}^+$, $C_2H_5{}^+$, and CH^-, C_2H^-, and Cl^- peaks.

3. Results and Discussion

3.1. Flotation Tests

Initially, the flotation tests were carried out to determine the effect of pulp pH on the flotation recovery of molybdenite and chalcopyrite. Figure 2 shows the floatability behavior of molybdenite and chalcopyrite as a function of pH with and without the use of a depressant reagent. As shown in Figure 2, without the addition of depressant, no selective separation effect was observed by pH, due to the natural hydrophobicity of both chalcopyrite and molybdenite [30]. These results are in good agreement with the studies carried out by Liu and Yin [5,10], in which it was shown that the flotation recovery of chalcopyrite and molybdenite are independent of pH. On the other hand, with the addition of thiocarbonohydrazide as a depressant, no depressant effect was observed on the recovery of the molybdenite as a function of pH due to its natural hydrophobicity. Furthermore, when pH was lower than 9, principally in the range of 4~8, there was no significant difference in the floatability of molybdenite with or without thiocarbonohydrazide (see Figure 2). This indicates that thiocarbonohydrazide has a limited effect on the hydrophobicity of molybdenite, and this is because there were no active sites for the adsorption of thiocarbonohydrazide. However, thiocarbonohydrazide significantly depressed the chalcopyrite floatability at concentrations of 4×10^{-3} M and pH values lower than 9. However, at the same concentrations of depressant, the floatability of chalcopyrite started increasing when the pulp pH increased to greater than 9 (see Figure 2). The higher floatability of chalcopyrite at higher pH can be explained by the decomposition of thiocarbonohydrazide and the better foaming properties of pulp slurry. It can be seen from Figure 2 that a substantial separation—greater than 70%—is obtained at pH 4~8, validating the effectiveness of thiocarbonohydrazide as a selective depressant for chalcopyrite at a solution concentration of 4×10^{-3} M.

As stated earlier, the aim of the present research is to evaluate the performance of thiocarbonohydrazide as a new environmentally friendly and selective depressant for chalcopyrite in order to replace the traditional toxic and hazardous reagents (which include cyanide, sodium sulphide and Nokes' reagent) in Cu-Mo flotation separation. Micro-flotation tests on pure minerals showed a minimal influence of TCH as a possible depressant in Mo-Cu separation. However, since the pure mineral flotation assessments alone weren't able to validate the adsorption of TCH on chalcopyrite and molybdenite, further extensive experiments were carried out on copper-bearing molybdenum bulk concentrate in the presence of both TCH and sodium sulphide to examine the potential of using TCH as an alternative selective depressant in copper-molybdenum separation. Figure 3 compares and contrasts the results of TCH and sodium sulphide as depressants in Cu-Mo separation. It can be seen from the results that, under the optimum dosage of 100 g/t (determined by the tests of reagent dosage), TCH attained a lower Cu recovery and similar Mo recovery, although the control test had significantly higher recovery for both. It seems that TCH has a negative effect on the flotation of molybdenite, which can be explained by the phenomenon whereby the surface tension of froth increased due to the introduction of TCH. These observations have attracted our attention, and more details will be presented in planned future work of the fundamental research.

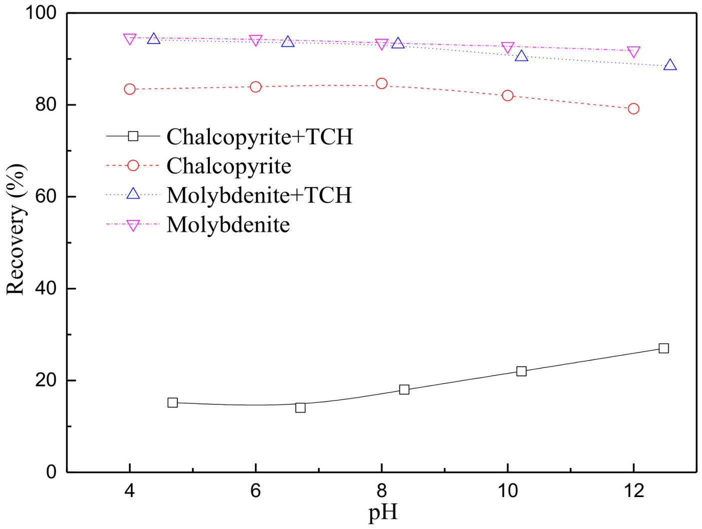


Figure 2. Influence of pH on floatability of chalcopyrite and molybdenite with or without thiocarbonohydrazide (4×10^{-4} mol/L), MIBC (80 mg/L) and Kerosene (200 mg/L).

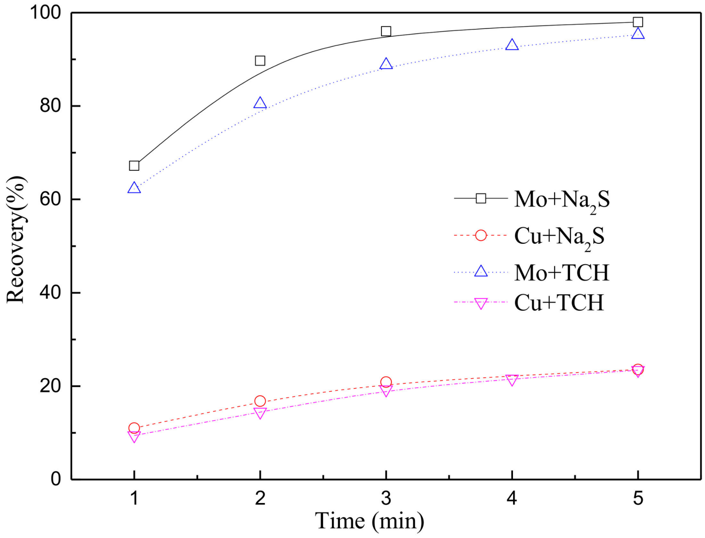


Figure 3. Flotation recovery of Cu and Mo at different flotation time with different depressants.

3.2. Zeta Potential Analysis

The zeta potential results given in Figure 4 show that chalcopyrite is negatively charged throughout the tested pH range, and it decreased continuously with increasing pH to about 10. However, the zeta potential started to maintain balance with further increase of pH higher than 10 (see Figure 4). The isoelectric point (IEP) of chalcopyrite was noted at about 5.00, which is in agreement with previously reported values [31,32]. Furthermore, it can be seen from these results that the zeta potential curve of chalcopyrite treated with the depressant followed a similar trend as pure chalcopyrite. However, the isoelectric point (IEP) of chalcopyrite treated with depressant was shifted to about pH 8.00, demonstrating that TCH had a strong influence on the zeta potential of chalcopyrite. TCH with two functional groups—thione (C=S) and primary amine (NH_2)—has a strong coordination ability to metal ions. In weak acidic medium, the main species of TCH exists in the protonated structure $[NH_2–NH–(C=S)–NH–NH_3]^+$, which might transform to $[NH_3–NH–(C=S)–NH–NH_3]^{2+}$, $[(NH_3)–NH–(C=S)–NH_2–NH_3]^{3+}$, or even $[(NH_3)–NH_2–(C=S)–NH_2–NH_3]^{4+}$, depending on the pH of the aqueous solution. In acidic medium, the addition of TCH has the effect of raising the zeta potential of chalcopyrite. This may be due to the reaction of chalcopyrite with the depressant. When TCH was adsorbed onto the surface of chalcopyrite, its functional group $NH_2–NH–(C=S)–NH–NH_2$ rearranged into $NH_2–N=(C–SH)–NH–NH_2$ [10]; then, the Cu ions bonded with S atoms to form complexes, while the S–H bonds were broken and released protons into the aqueous solution. Under alkaline conditions, the thione group of TCH can exhibit tautomerism to thiol, forming $[NH_2–N=(C–SH)–NH–NH_2]$ structure, and react with OH^- to form $[NH_2–N=(C–S)–NH–NH_2]^-$, which could strongly adsorb onto the chalcopyrite surface, shifting the zeta potential of the chalcopyrite to a more negative value. Interestingly, results obtained are in great agreement with those of the micro-flotation measurements.

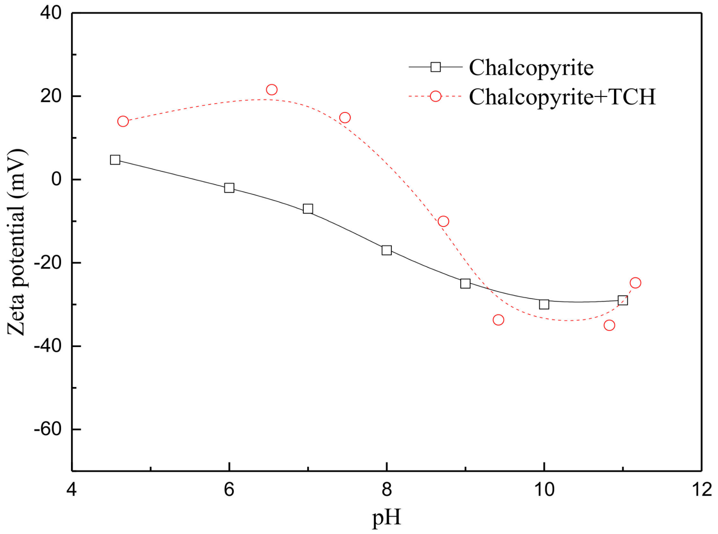


Figure 4. Zeta potential measurements of pure chalcopyrite as a function of pH in presence and absence of TCH (2×10^{-4} M/L).

3.3. FTIR Spectra Measurements

FTIR spectroscopy was adopted to characterize TCH, $TCH–Cu^{2+}$ complexes, chalcopyrite in the presence and absence of TCH solution. As illustrated in Figure 5, the characteristic peaks developed at around 3306 or 3274 cm^{-1} decreased or even disappeared in the $TCH–Cu^{2+}$ complexes, demonstrating that some N-H bonds [33] of TCH might break during the formation of $TCH–Cu^{2+}$ complexes. The thiol (S–H)-stretching vibrations developed at 2770 cm^{-1} also disappeared in $TCH–Cu^{2+}$ complexes, demonstrating the formation of a Cu–S bond. Meanwhile, the strong peaks at around 1530 and 1490 cm^{-1} for the N–C(=S)–N–N complex vibrations in the TCH molecule were shifted to 1510 and 1385 cm^{-1} in the $TCH–Cu^{2+}$ complexes, respectively, informing the interaction of copper with sulphur and nitrogen atoms. The difference in FTIR spectra between the TCH and $TCH–Cu^{2+}$ complexes suggests that when TCH is reacted with Cu^{2+} ions, its functional group $NH_2–NH–C(=S)–NH–NH_2$ rearranges to $NH_2–NH–C(–SH)=N–NH_2$; then, the copper ions bond with sulphur and nitrogen atoms to make Cu–S and Cu–N bonds by the breaking of S–H bonds. The results show that, after treatment with TCH, new peaks developed on the chalcopyrite surface at around 592, 1079, 1140, 1285 and 1327 cm^{-1} due to $TCH–Cu^{2+}$ complexes also appearing on chalcopyrite. Therefore, a conclusion could be drawn that TCH might chemisorb onto the chalcopyrite surface due to the formation of $TCH–Cu^{2+}$ complexes, which is in line with the observations of ATDT–Cu [2], AHS–Cu [10] and HATT–Cu complexes [34].

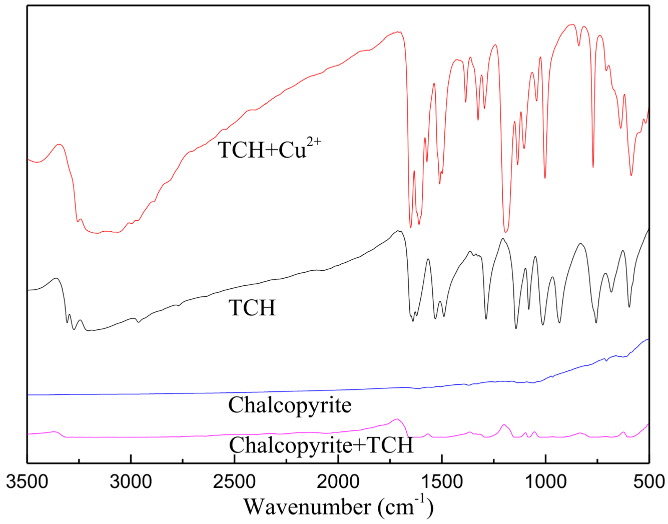


Figure 5. FTIR spectra of TCH, TCH–Cu^{2+} complexes and chalcopyrite treated and untreated with TCH.

3.4. XPS Analysis

XPS is known to be a very useful surface analytical tool for explaining the interaction mechanism between reagents and minerals. In the present study, XPS examinations provide evidence regarding the surface species formed by the interaction of TCH molecules with chalcopyrite. The survey scan spectra of TCH and chalcopyrite before and after treatment with TCH are shown in Figure 6. Figure 6 clearly displays the presence of component elements, such as S, C, N, and no any indication of impurities by other elements can be found. The atomic concentrations of chalcopyrite with and without TCH treatment are listed in Table 1. Table 1 indicates that the atomic concentrations of the C and N atoms on the chalcopyrite surface increases with TCH treatment, while those of the O, S, Fe and Cu atoms decreases, which further confirms the TCH adsorption onto the chalcopyrite surface.

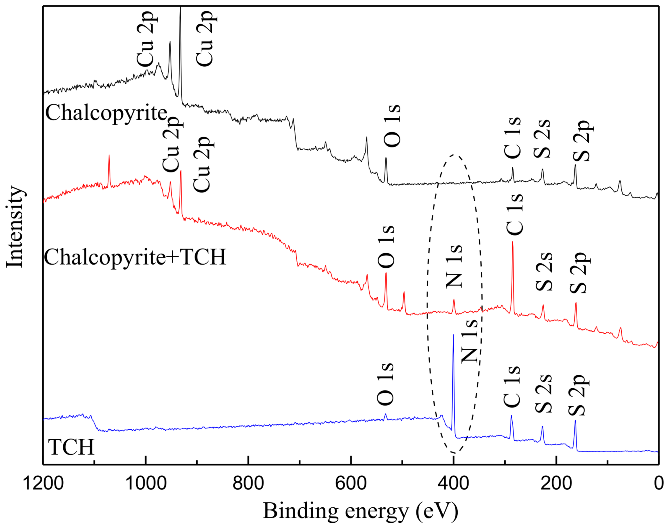


Figure 6. XPS spectra of TCH and chalcopyrite with and without treatment.

Table 1. Element contents of chalcopyrite with and without treatment.

Samples	Atomic Concentration (%)					
	C	O	N	S	Cu	Fe
chalcopyrite	25.45	20.73	0.00	27.48	18.98	7.36
chalcopyrite + TCH	60.91	11.49	7.77	12. 93	4. 71	2.18
Δ^a	35.46	−9.24	7.77	−14.55	−14.27	−5.18

Δ^a is defined as the value after TCH treatment minus than that of the original.

The high-resolution sulphur 2p spectra of the TCH, TCH–Cu complexes, as well as chalcopyrite with and without treatment with depressant, were collected and are displayed in Figure 7. The S 2p XPS spectra of chalcopyrite can be fitted by four components at around 161.41 eV (originating from bulk monosulphide), 162.59 eV (disulphide species) and 164.02 eV (Sn^{2-}/S^0), these features are in agreement with previous reports [35,36]. Another S 2p peak centered at 169.25 eV is assigned to sulphate species, which demonstrates the oxidation of chalcopyrite surface [35]. The S 2p XPS spectra of TCH, TCH–Cu complexes and chalcopyrite adsorbed with TCH were composed of two components. The S 2p XPS spectra of TCH is quite similar to that of HATT, with BE at 162.12 and 164.47 eV, which is derived from the thione sulphur of C=S functional group and the thiol sulphur of C–SH group [37,38]. The S 2p spectrum of TCH–Cu precipitates is composed of two components located at around 162.27 and 163.75 eV, which were likely derived from the thiolate S species of TCH–Cu precipitates and the oxidation state S of TCH [37,38]. After treatment with TCH, the S 2p XPS spectra of the chalcopyrite surface was divided into two components centered at 162.15 and 164.04 eV, which are likely derived from the thiol S of the Cu–S species in the TCH–Cu surface complex and the oxidation state S of TCH. Therefore, a conclusion could be drawn that a new Cu–S bond might be formed after the adsorption of TCH on the chalcopyrite surface.

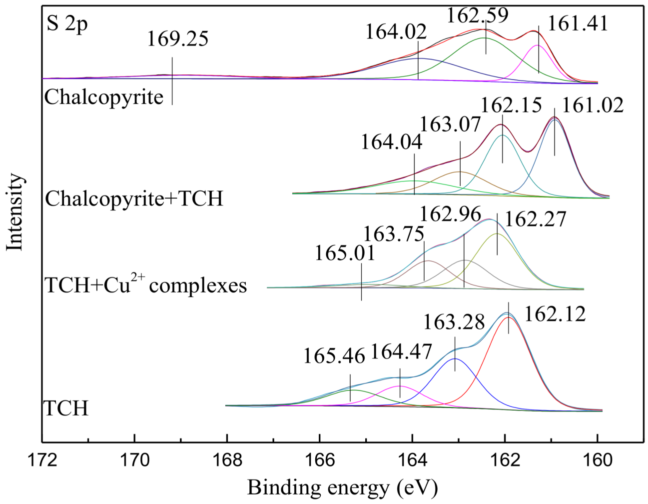


Figure 7. S 2p spectra of TCH, TCH–Cu^{2+}, and chalcopyrite before and after treatment.

Figure 8 shows the N 1s XPS spectra of TCH, TCH–Cu complexes and TCH-treated chalcopyrite. It is clear that the N 1s XPS spectrum of TCH is divided into two components at around 400.94 and 400.10 eV, which were assigned to the nitrogen atoms of primary and secondary amine of –NH–(C=S)–NH– and –NH_2 groups, respectively. The N 1s spectrum of the TCH–Cu complexes was divided into three components. The main band located at around 399.45 eV is likely derived from the C–N–N group, which has been reported to be 399.12 eV [38]. The higher binding energy components at 400.64 and 400.32 eV were attributed to Cu–N and C=N, respectively. These findings indicate the formation of a Cu–N bond during the TCH reaction with copper ions, which is in good agreement with the findings of X-ray single crystal and HATT–Cu complexes [26,38,39]. After the adsorption of TCH, N 1s XPS bands at around 398.79, 399.85 and 400.57 eV appeared on the chalcopyrite surfaces, which were assigned to the nitrogen species C–N–N, C=N and Cu–N, respectively [37]. Observations of binding energies obtained from chalcopyrite covered with TCH are very similar to the values given by the TCH–Cu complexes, thus confirming the nitrogen contribution for the formation of metal complexes on the chalcopyrite surface.

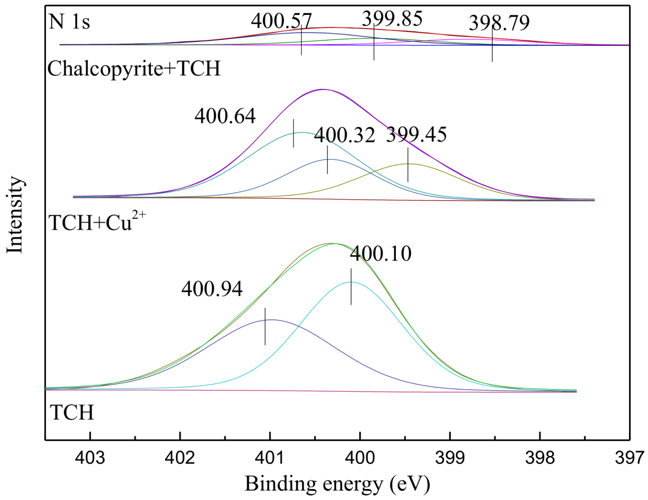


Figure 8. N 1s spectra of TCH, TCH–Cu^{2+} and chalcopyrite after treatment.

It is widely acknowledged that the Cu 2p binding energy of copper dichloride can be divided into two components centered at 933.89 and 953.99 eV [10], which are shifted to a lower binding energy in TCH–Cu^{2+} complexes by 1.55 and 1.77 eV, respectively, indicating that the electron density of copper ions has increased due to the coordination of S and N atoms to copper ions. As can be seen in Figure 9, the Cu 2p binding energy of chalcopyrite was observed at around 932.40 and 952.30 eV, representing Cu 2p3/2 and Cu 2p1/2 of chalcopyrite, respectively, and these values are in line with the results reported in the literature [36,40]. After TCH treatment, both Cu 2p3/2 and Cu 2p1/2 of chalcopyrite shifted to lower binding energies by 0.73 and 0.78 eV, respectively, indicating the adsorption of TCH on chalcopyrite by formation of TCH–Cu complexes on the chalcopyrite surface. These findings, to some extent, are in agreement with the observation of HATT bond copper atoms with its N and S atoms on the chalcopyrite surface by the formation of HATT–Cu complexes [34].

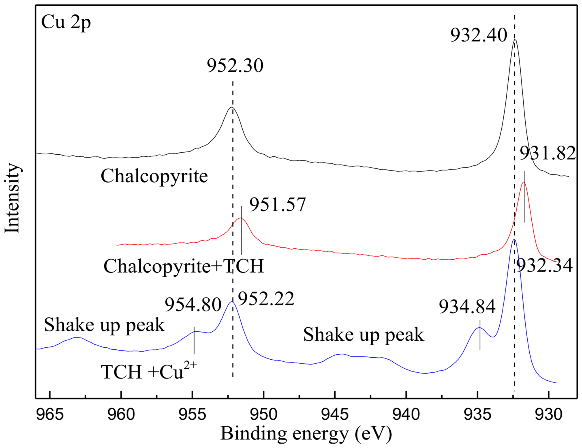
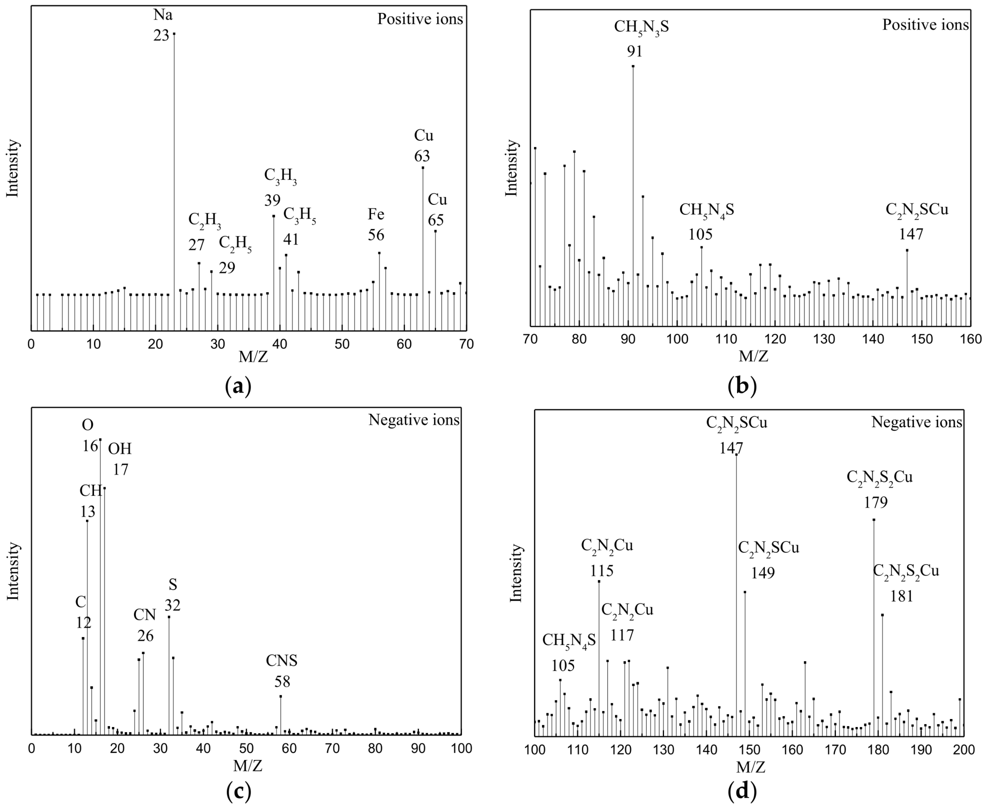


Figure 9. Spectra of TCH+Cu^{2+} complexes, chalcopyrite before and after treatment.

3.5. ToF-SIMS Analysis

Time of flight-secondary ion mass spectrometry (ToF-SIMS) is considered a particularly valuable technique, due to its spatial resolution, high mass spectral and sensitivity capabilities [41]. It has been used for a long time to identify the mechanisms of surface interaction between minerals and flotation reagents [42–44]. In this investigation, ToF-SIMS measurements were carried out to characterize the chalcopyrite surface after TCH adsorption. Figure 10 demonstrates the negative-ion (c and d) and positive-ion (m/z 1–400) spectra (a and b). During the measurements, all spectra were run under high-resolution conditions, but only high-intensity fragments for all the elements were recorded. In the positive-ions spectra, possible heteroatom ions detected in m/z range of 0–200 were Na^+ (m/z 23), $C_2H_3{}^+$ (m/z 27), $C_2H_5{}^+$ (m/z 29), $C_3H_3{}^+$ (m/z 39), $C_3H_5{}^+$ (m/z 41), Fe^+ (m/z 56), $^{63}Cu^+$ (m/z 63), $^{65}Cu^+$ (m/z 65), $CH_3N_3S^+$ (m/z 91), $CH_5N_4S^+$ (m/z 105) and $C_2N_2S^{63}Cu^+$ (m/z 147). The negative ions in the m/z range of 0–400 were C^- (m/z 12), CH^- (m/z 13), O^- (m/z 16), OH^- (m/z 17), CN^- (m/z 26), S^- (m/z 32), CNS^- (m/z 58), $CH_5N_4S^-$ (m/z 105), $C_2N_2{}^{63}Cu^-$ (m/z 115), $C_2N_2{}^{65}Cu^-$ (m/z 117), $C_2N_2S^{63}Cu^-$ (m/z 147), $C_2N_2S^{65}Cu^-$ (m/z 149), $C_2N_2S_2{}^{63}Cu^-$ (m/z 179) and $C_2N_2S_2{}^{65}Cu^-$ (m/z 181). The results for positive and negative ions clearly indicate that after interacting with TCH, the molecular fragments of both TCH and TCH–Cu complexes were present the chalcopyrite surface. Moreover, the fragments of TCH–Cu complexes such as $C_2N_2S^{63}Cu^+$ (m/z 147), $C_2N_2S^{63}Cu^-$ (m/z 147), $C_2N_2S^{65}Cu^-$ (m/z 149), $C_2N_2S_2{}^{63}Cu^-$ (m/z 179) and $C_2N_2S_2{}^{65}Cu^-$ (m/z 181) that appeared on the chalcopyrite surface further confirmed that TCH might have bonded with Cu ions through sulphur (SH) and nitrogen (NH_2) atoms by the formation of five-member chelating rings. The absence of TCH-Fe fragments in the ToF-SIMS spectra should be noted, indicating that TCH prefers to adsorb onto Cu rather than Fe atoms. Therefore, the dominant adsorption sites of TCH on the chalcopyrite surface were Cu atoms, rather than Fe atoms.

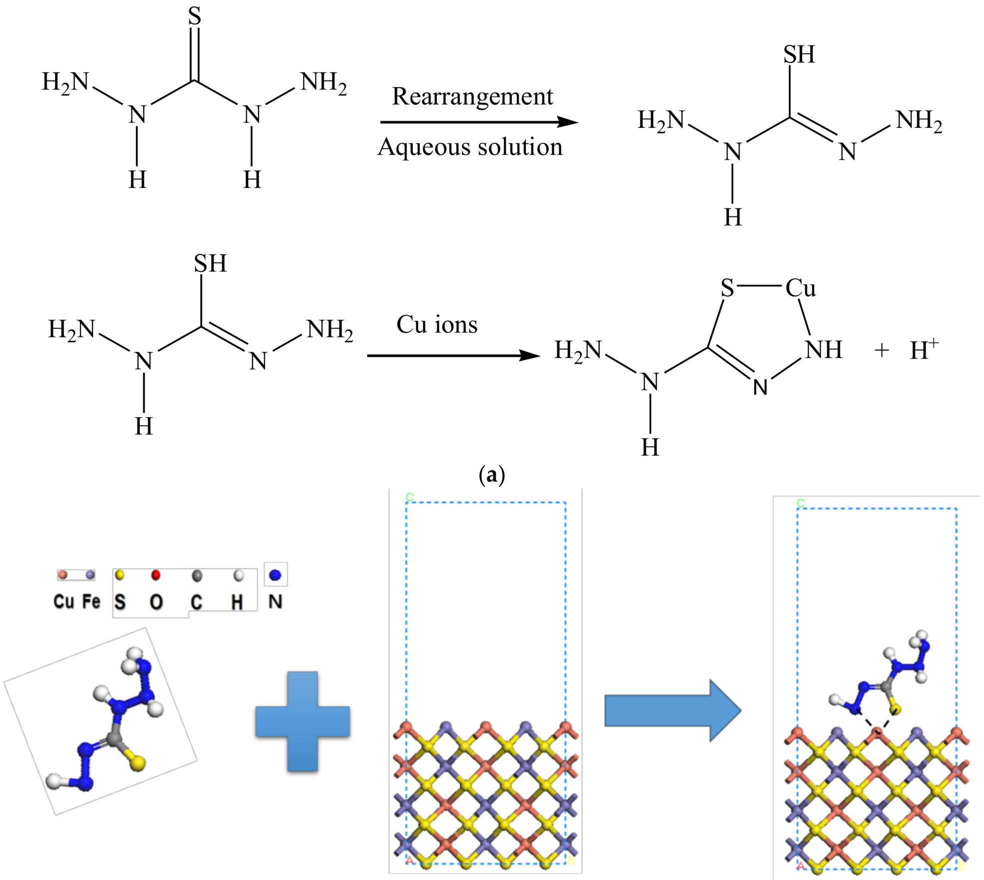


(**a**) (**b**) (**c**) (**d**)

Figure 10. ToF-SIMS spectra of chalcopyrite surface after adsorption of thiocarbonohydrazide, (**a**,**b**) negative-ions; and (**c**,**d**) positive-ions spectra.

3.6. Adsorption Model

TCH, as an amphoteric substance, can exist as a protonated structure or anionic species at different pH values. As a result, after adsorption of the isomer of TCH, the zeta potential of chalcopyrite varies with pH. The results of FTIR suggested that TCH might chemisorb on the surface of chalcopyrite through its rearranged functional group NH_2–NH–C(–SH)=N–NH_2 to make complexes on chalcopyrite surface. The results of XPS and ToF-SIMS analysis further demonstrated that TCH reacts with copper atoms through its nitrogen and sulphur atoms to form five-membered chelating rings. On the basis of the results discussed above, an adsorption model of TCH on chalcopyrite surfaces was proposed, which is shown in Figure 11.



(**a**)

(**b**)

Figure 11. (**a**) Rearrangement of functional group NH_2–NH–C(–SH)=N–NH_2 and formation of complexes on chalcopyrite surface; (**b**) proposed chemisorption model of TCH on chalcopyrite surfaces.

4. Conclusions

In this work, a new surfactant thiocarbonohydrazide (TCH) was successfully synthesized and utilized as a selective depressant for chalcopyrite in the flotation separation of molybdenite and chalcopyrite. Various flotation tests, as well as measurements of zeta potential, FTIR spectra, XPS and ToF-SIMS were performed to analyze and interpret the adsorption behaviors and mechanisms of TCH on the chalcopyrite surface. Based on the investigation findings, the following main conclusions can be drawn:

(a) Flotation results indicated that TCH has a strong depressive strength and selectivity towards chalcopyrite and a negligible effect on the floatability of molybdenite at pH lower than 9.

(b) Zeta potential measurements showed that the adsorption between TCH and chalcopyrite is chemisorption, and results into the formation of TCH–copper complexes. Further, after TCH treatment, the surface of chalcopyrite becomes more positively charged in the pH ranges from 4 to 8. The positive charges can be attributed to the protonated isomer structure of TCH, implying stronger interactions with copper ions.

(c) FTIR analysis displayed the appearance of new vibrational bands on the chalcopyrite surface due to TCH–Cu^{2+} complexes, which were probably produced by the reaction of thiol and primary amine functional groups of TCH with copper atoms to form Cu–S, Cu–N bonds on the chalcopyrite surface.

(d) Results of XPS and ToF-SIMS measurements further confirmed the chemisorption of TCH onto the chalcopyrite surface.

(e) Based on this detailed investigation, it is suggested that thiocarbonohydrazide (TCH), due to its unique properties, such as double chelating groups, characteristic adsorption manner, good selectivity, environmental friendliness, etc., could be used as a good depressant for chalcopyrite in the flotation separation of molybdenum sulphide minerals.

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