

## Enhanced sulfidation of chrysocolla with ammonium carbamate and its effect on flotation

Ziang Wang, Dandan Wu, Jing Cao, Huiqin Chen

State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, PR China

Corresponding author: [wdd1006530@sina.com](mailto:wdd1006530@sina.com) (Dandan Wu)

**Abstract:** In this study, flotation experiments, zeta potential, XPS, AFM, SEM-EDS, and contact angle measurements were performed to study the influence of ammonium carbamate ( $\text{CH}_6\text{N}_2\text{O}_2$ ) on the sulfidation flotation of chrysocolla. The results of the sulfidation flotation experiments showed that the recovery of chrysocolla increased more than 40% on the optimal condition after adding ammonium carbamate. In addition, the zeta potential of samples with ammonium carbamate was clearly higher than ores for  $\text{pH} > 6$ , which was due to the complexation reaction between ammonium carbamate and copper ion on the surface of chrysocolla samples. The activity of copper adsorption has also been improved. Furthermore, the XPS data indicated that the content of Cu-S compounds on the mineral surface has been significantly enhanced after ammonium carbamate complex sulfidation. The chemical analysis of the solution led to the same conclusion. The AFM results showed that ammonium carbamate had a positive impact on the adsorption of minerals surface, and increased the flotation recovery. It can be deduced from the SEM-EDS analysis that the surface of chrysocolla better combined with S<sup>-</sup>, and more Cu-S components were generated on the surface, which led to 1.04% increase of S atomic concentration. Finally, the contact angle measurements showed that the water contact angle of chrysocolla after adding ammonium carbamate could reach 90.4°, which proved that the sulfidation improved the floatability of the chrysocolla sample.

**Keywords:** chrysocolla, ammonium carbamate, surface modification, sulfidation

### 1. Introduction

Copper, as a kind of nonferrous metal, plays an important role in the national economy and industry (Wang et al. 2010; Tanaydin et al. 2022; Leandro et al. 2012; Zhang et al. 2012). However, the worldwide production of copper is recently stagnating (Manuela et al. 2022). Therefore, it is crucial to find new copper mineral sources, and to develop more efficient production technologies. It is known that sulfide ore is the main source of copper minerals. Due to the overexploitation of sulfide ore, copper oxide ore has been widely used in the production to respond to the industry demand (Han et al. 2017). However, the flotation of copper oxide ore with xanthate collectors is difficult because of the hydrophilic surface. Several methods were developed to utilize copper oxide ore, such as flotation (Yu et al. 2021), hydrometallurgy (Clotilde Apua et al. 2021), and pyrometallurgy (Zhang et al. 2012).

Chrysocolla, whose chemical composition is generally considered as  $\text{Cu}_{2-x}\text{Al}_x(\text{OH})_4\text{H}_2\text{-xSi}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  ( $x < 1$ ), is a copper silicate mineral with high industrial value (Hope et al. 2012; Frost et al. 2013; Bideaux et al. 1995). Its resource is second to malachite in copper oxide minerals, and its copper content can generally reach 35%. However, chrysocolla is usually discarded in the conventional flotation process. This is due to the technical difficulties in the recycling of wollastonite. More precisely, the structure of chrysocolla is quite complex, and it is difficult to separate it by conventional separation approaches. The study of Raghavan and Fuerstenau (Raghavan & Fuerstenau, 1977) mentioned that the challenges encountered in the practical flotation of chrysocolla were attributed to its microporous structure, which is mainly formed by cupric hydroxide, amorphous silica, and water. In addition, because of its form of amorphous minerals with a complex surface structure, most of the

flotation collectors lack the selectivity for chrysocolla, and therefore it is difficult to separate it from gangue.

At present, the commonly used recovery methods of chrysocolla can be divided into (1) acid leaching or ammonia leaching, (2) direct flotation, and (3) modified flotation.

Acid leaching has good recovery effect on chrysocolla. However, the acid can react with impurities in gangue minerals because of its poor selectivity, which will result in increasing the need of acid (Banza et al. 2003). Ammonia leaching usually requires high-temperature treatment, which consumes lot of energy, and the recovery process is slow (Habashi et al. 1973). The collector used in direct flotation has poor selectivity to chrysocolla, and thus it is difficult to separate it from gangue minerals. Therefore, modified flotation, especially the sulfide xanthate method, is considered as one of the most promising processes for the recovery of chrysocolla (Alpan et al. 1984; Guo et al. 2021).

However, the adsorption capacity of sulfide on the surface of chrysocolla is low because of its complex surface structure, which results in the difficulty of normal sulfidation flotation of chrysocolla (Raghavan et al. 1984). Heating was proved to be efficient for solving this problem. However, an excessive energy consumption decreases the feasibility in industrial production (Parks et al. 1966). In this condition, the modification on the surface of chrysocolla to generate a stable copper sulfide film is thought to be crucial for sulfidation flotation. A study on the ammonia modification of the surface of minerals has been conducted (Wu et al. 2017; Dong et al. 2021).

Shen et al. studied the application mechanism of ammonium phosphate in the sulfidation flotation of chrysocolla (Shen et al. 2020). The obtained results showed that ammonium phosphate has a certain activation effect on the flotation of chrysocolla. It can also be deduced from the obtained results that chrysocolla changed from a non-floating state to an easily floating state when the concentration of ammonium phosphate is appropriate, while an excess concentration of ammonium phosphate has a negative impact on the sulfidation flotation of chrysocolla. The reaction mechanism of ammonium phosphate in the sulfidation flotation of chrysocolla may takes a part in the liquid-solid chemical reaction between the  $\text{Na}_2\text{S}$  solution and chrysocolla. This produces the stable adsorption of crystalline copper sulfide on the surface of chrysocolla, and improves the flotation behavior.

This study aims at investigating the use of  $\text{CH}_6\text{N}_2\text{O}_2$  as a corrosion activator in the flotation separation of chrysocolla and quartz by sulfidation-xanthate flotation through micro flotation. In addition, the  $\text{CH}_6\text{N}_2\text{O}_2$  corrosion activation of chrysocolla was studied by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), in order to investigate the mechanism of  $\text{CH}_6\text{N}_2\text{O}_2$  in sulfidation flotation.

## 2. Materials and methods

### 2.1. Materials and reagents

The samples used in the experiments were from Yunnan Province, China. Gangue minerals in ores were removed by artificial crushing to obtain a relatively pure chrysocolla sample. The next procedure consists in grinding the massive chrysocolla using an agate three-head grinder. The ground chrysocolla powder samples were screened with a standard sieve to obtain powder samples with different particle sizes. The chrysocolla powder having a particle size in the range of ( $-74 \mu\text{m} + 47 \mu\text{m}$ ) was considered as the sample for the flotation experiment. The XRD analysis results of the chrysocolla sample are shown in Fig. 1. The chemical composition analysis is presented in Table 1. The contents of Cu,  $\text{Al}_2\text{O}_3$ , CaO, and Fe in the chrysocolla were determined by EDTA titration, while the content of Si (calculated by  $\text{SiO}_2$ ) was determined using the potassium fluosilicate volumetric method.

Table 1. Chemical composition of chrysocolla

Composition	Cu	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	CaO	Fe
Content (%)	34.25	33.38	1.35	0.41	0.50

### 2.2. Microflotation tests

The flotation experiments used an XFG flotation machine with a flotation cell volume of 50 ml. A 2 g chrysocolla sample having a particle size in the range of ( $-74 \mu\text{m} + 47 \mu\text{m}$ ) was weighed and added to

the flotation cell, then continuous stirring was performed for 1 min. A  $\text{CH}_6\text{N}_2\text{O}_2$  solution with different concentrations was first added to the pulp, and reacted for 5 min. The freshly prepared  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  solution and Sodium isoamyl Xanthate (NaIX) solution were then sequentially added for sulfidation and flotation of the chrysocolla sample, and both were for 5 min. These flotation experiments were conducted with natural pH, in order to study the effect of  $\text{CH}_6\text{N}_2\text{O}_2$  in the sulfidation flotation of chrysocolla. The concentrate and tailings were filtered, dried, and weighed after each experiment. Finally, the recovery was calculated using the data.

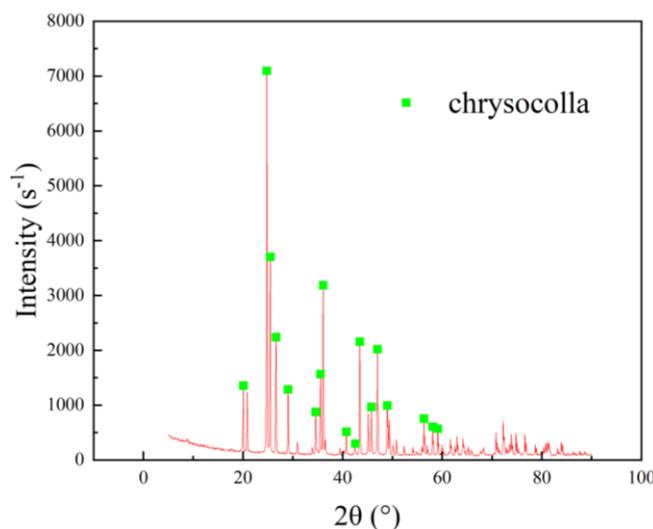


Fig. 1. XRD pattern of the chrysocolla

### 2.3. Zeta potential measurements

The Zeta potential of the samples was measured, before and after the experiments, using a potential analyzer. Before the measurement of the Zeta potential, the chrysocolla sample was ground to finer than 5  $\mu\text{m}$ . The electrolyte solution was a KCl solution having a concentration of  $3 \times 10^{-3}$  mol/L. The Zeta potential measurements used 50.0 mg of chrysocolla sample, 50 ml of deionized water and reagents having similar concentration to those in the flotation experiments. NaOH and  $\text{H}_2\text{SO}_4$  were then used to adjust the pH of the solution. Afterwards, flotation reagents were added in the above order while magnetically stirring at 500 r/min. Finally, the pulp was stood for 5 min, and the supernatant was extracted and placed into a Malvin electrode to measure the Zeta potential.

### 2.4. XPS measurements

X-ray photoelectron spectrometry was used for the surface analysis of chrysocolla after sulfidation. The sample was produced by chrysocolla powder. The order of adding reagents was consistent with that of the flotation experiments. After filtration, the mineral samples were dried in a vacuum at 40°C and then sealed. XPS was performed as quickly as possible to prevent the oxidation of the sample. Using Mg-K $\alpha$  X-ray excitation, the X-ray source power was 200 W, the background vacuum was greater than  $10^{-7}$  Pa, and the energy scale was corrected to the binding energy of contaminant carbon C 1s at 248.8 eV. The XPS data were analyzed using the MultiPak software. The analysis includes peak fitting and semi-quantitative analysis.

### 2.5. AFM measurements

AFM was used to obtain the two-dimensional geometric morphology and three-dimensional height morphology of chrysocolla under various conditions. A Bruker Dimension Icon, having a mineral scanning range of 5  $\mu\text{m} \times 5 \mu\text{m}$ , was used. The samples were prepared using chrysocolla powder, which was dispersed in water until the mixture became transparent, and the order of the added reagents was consistent with that of the flotation experiments. Afterwards, it was dropped onto a clean mica sheet, then dried and tested.

## 2.6. SEM-EDS measurements

The surface morphology and energy spectrum of the chrysocolla samples were tested under different conditions. The Tescan MIRA4 instrument was used. A small amount of chrysocolla sample powder was removed and adhered to a conductive adhesive, and excess powder was blown away from the sample table using an ear washing ball. The sample was placed in a gold-spraying instrument and plated with gold, then placed in the SEM. The SEM analysis was performed under an accelerating voltage of 15 keV, a beam current of 100 pA, a working distance of 15 mm, and under vacuum.

## 2.7. Contact angle measurements

In this study, the JY-82 contact angle goniometer was used to measure the water contact angle (WCA) of the chrysocolla sample before and after flotation. The specific testing procedure is as follows. The pure chrysocolla sample was first ground into a thin slice to achieve a high degree of flatness on one side. The ground slice of chrysocolla was then placed in a beaker with 40 mL of deionized water. The pH was adjusted to 9, and the dosages of NaIX,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , and ammonium carbamate were set to  $1.5 \times 10^{-3}$  mol/L,  $1.5 \times 10^{-3}$  mol/L, and  $8 \times 10^{-3}$  mol/L, respectively. The flotation reagents were added and stirred according to the flotation agent system and process. After the chrysocolla slices were naturally air-dried, the contact angle test was performed.

## 3. Results and discussion

### 3.1. Microflotation studies

Fig. 2 shows the curves of the flotation experiments with different concentrations of reagents, in which the flotation recovery is the ordinate while the NaIX concentration of the solution is the abscissa. The conditions of the curves were  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  ( $1.5 \times 10^{-3}$  mol/L) and  $\text{CH}_6\text{N}_2\text{O}_2$  ( $8 \times 10^{-3}$  mol/L) +  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  ( $1.5 \times 10^{-3}$  mol/L).

In the flotation experiments which used  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  ( $5 \times 10^{-4}$  mol/L) as the sulfidation agent, the data demonstrated that the flotation recovery of chrysocolla samples increased from 23.67% to 38.30% when the concentration of NaIX increased from  $1 \times 10^{-3}$  mol/L to  $5 \times 10^{-3}$  mol/L. When the concentration of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  was  $1.5 \times 10^{-3}$  mol/L, the flotation recovery of chrysocolla samples increased from 45.70% to 80.36% with the increase of the concentration of NaIX from  $1 \times 10^{-3}$  mol/L to  $5 \times 10^{-3}$  mol/L. The results showed that the recovery of chrysocolla samples has been greatly improvement. This may be due to the complexation reaction between copper ion and  $\text{CH}_6\text{N}_2\text{O}_2$  on the chrysocolla surface, which increased the activity of copper adsorption on the surface. Therefore, more  $\text{S}^{2-}$  is adsorbed on the surface of chrysocolla, and more copper-sulfide components are generated.

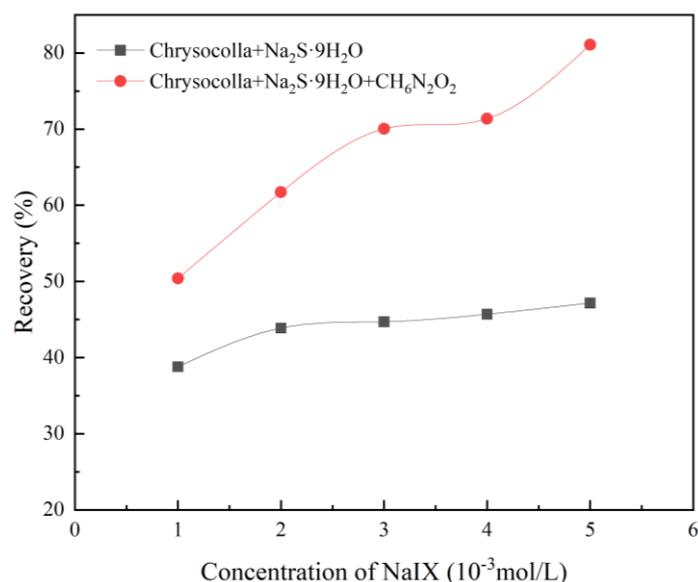


Fig. 2. Effect of NaIX concentration on flotation recovery of chrysocolla

### 3.2. XPS analysis

XPS is an important surface analysis method which can detect the state of elements in the depth range of 2 nm. It is used to study the elemental components and their chemical valence states on solid surfaces (Han et al. 2020; Feng et al. 2019). The general principle of XPS analysis is as follows. X-rays are used to irradiate the mineral sample in the X-ray photoelectron spectrometry, causing the inner-shell or valence electrons of the atoms or molecules to be excited and ejected. The electrons excited by photons are referred to as photoelectrons, whose energy can be measured. By plotting the relative intensity against the kinetic energy of the photoelectrons, a photoelectron energy spectrum can be obtained and used to determine the composition of the sample.

In this paper, XPS analysis of chrysocolla, before and after sulfidation, was conducted to study the influence of the reagents on the flotation. Fig. 3 shows the XPS full scan spectra of the chrysocolla samples under different conditions, in which Cu, S, O, Si, and other elements are detected. Table 2 presents the atomic concentration on the surface of chrysocolla under various reagent conditions. It can be clearly seen from Table 2 that the atomic concentration of O decreases after direct sulfidation, the atomic concentration of Cu slowly decreases under the same condition, the atomic concentration of Si almost remains unchanged, while the atomic concentration of S increases. The results showed that the combination of S and Cu is more difficult than the combination of S and O, which impedes the direct sulfidation of chrysocolla.

Fig. 3 and Table 2 show that the atomic concentration of S on the chrysocolla surface after complex sulfidation with  $\text{CH}_6\text{N}_2\text{O}_2$  was 0.9%, while that after direct sulfidation was less than 0.1%. As for O, the atomic concentration after  $\text{CH}_6\text{N}_2\text{O}_2$  complex sulfidation was 69.1%, while that after direct sulfidation was 65.2%. The atomic concentration of Cu on the chrysocolla surface after  $\text{CH}_6\text{N}_2\text{O}_2$  complex sulfidation was 6.1%, while that after direct sulfidation was 7.9%. This may be due to the micro-dissolution of chrysocolla surface by  $\text{CH}_6\text{N}_2\text{O}_2$ , which increases the sulfidation efficiency and the flotation recovery of chrysocolla.

Figs. 4(a), and 5(a) show the O 1s and Cu 2p XPS spectra of chrysocolla samples. It can be deduced from the literature that the O 1s peak at 530.70 eV was CuO (Firsov et al. 1982) and the peak at 532.78 eV was  $\text{SiO}_2$  (Venezia et al. 1995). In addition, the Cu 2p  $3/2$  peak at 934.79 eV was corresponding to CuO (Haber et al. 1978), and the peak at 936.00 eV was  $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$  (Nakai et al. 2007). Furthermore, the Cu 2p  $1/2$  peak at 955.96 eV was also CuO (Geesey et al. 2005), and the Si 2p peak at 102.08 eV was (-Si-O) (Zuo et al. 2020). The peak of S 2p in the chrysocolla samples cannot be found in Fig. 7, which indicates that there is no S in ores.

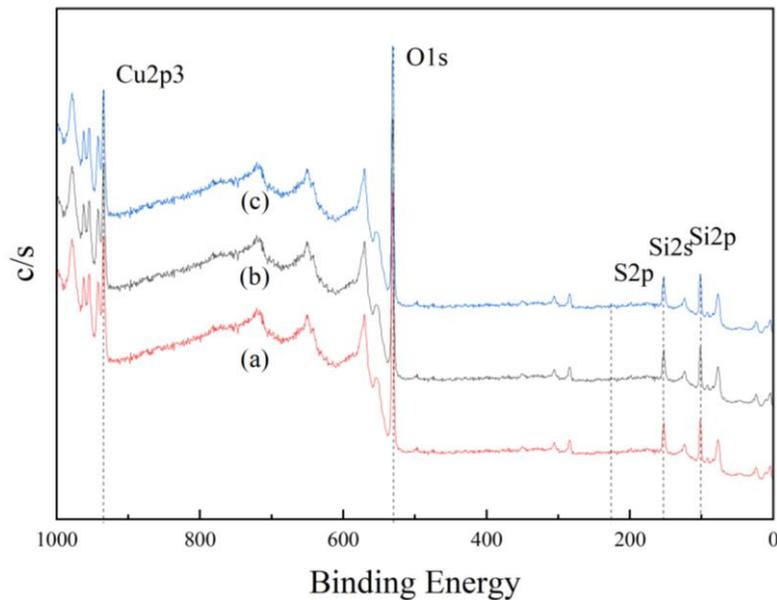
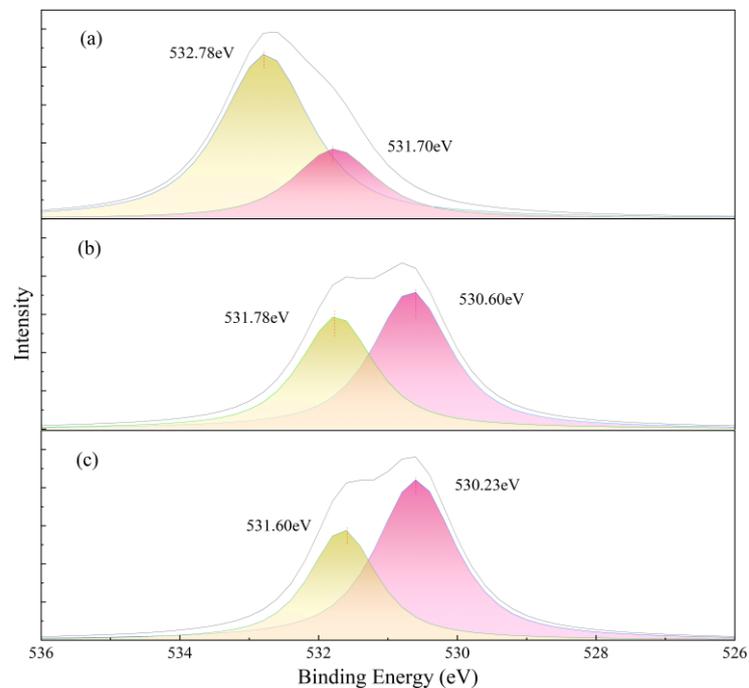
The O 1s and Cu 2p XPS spectra of chrysocolla after direct sulfidation are shown in Figs. 4(b) and 5(b). The O, Cu, and Si peaks shifted, compared with those of the pure chrysocolla, and the peak of S appeared, which indicates that there are changes on the element composition and state on the chrysocolla surface after direct sulfidation. The O 1s of CuO and  $\text{SiO}_2$  species shifted to 530.23 eV and 531.60 eV. There is still no peak of S. In addition, compared with pure chrysocolla ores, the content of Si decreased due to the dissolution of Si on the chrysocolla surface. There are two pairs of fitted peaks of Cu 2p. The former peak is 934.28 eV (2p  $3/2$ ), which is considered as  $\text{CuSiO}_2(\text{OH})_2$  (Nakai et al. 1978), while the latter peak at 932.60 eV (2p  $3/2$ ) is CuO, and the peak at 955.80 eV (2p  $1/2$ ) proved the obtained result (Folmer et al. 1980).

Figs. 4(c), 5(c) and 6 show the O 1s, Cu 2p, and S 2p XPS spectra of chrysocolla after complex sulfidation with  $\text{CH}_6\text{N}_2\text{O}_2$ . It can be seen that the binding energy of O 1s is higher than that of direct sulfidation. There is a pair of fitted peaks of S 2p in Fig. 6(b) at 162.11 eV and 160.61 eV, corresponding to CuS. Moreover, the area of S 2p is clearly larger than that of direct sulfidation in Fig. 6(a), which indicates that  $\text{CH}_6\text{N}_2\text{O}_2$  facilitated the sulfidation of chrysocolla. In fact,  $\text{CH}_6\text{N}_2\text{O}_2$  and Cu on the chrysocolla surface led to a complexation reaction, which changed the distribution of elements. The Cu 2p was fitted to two pairs of peaks. The binding energy of the former peak is 935.64 eV (2p  $3/2$ ), while those of the latter peaks are 933.15 eV (2p  $3/2$ ) and 952.30 eV (2p  $1/2$ ). They correspond to  $\text{CuSiO}_2(\text{OH})_2$  and  $\text{CuS}_x$  ( $x=1,2$ ) (Brion, 1980), respectively.

It can be deduced from the XPS analysis that the existence of  $\text{CH}_6\text{N}_2\text{O}_2$  has a positive impact on the sulfidation flotation of chrysocolla by producing hydrophobic Cu-S compounds, which increased the surface sulfidation activity of chrysocolla and improved its sulfidation-xanthate flotation.

Table 2. Semi-quantitative analysis of surface atomic concentration of chrysocolla

sample	C	O	Si	S	Cu
	atomic concentration (%)				
chrysocolla	6.3	68.6	18.0	0	7.0
chrysocolla+Na <sub>2</sub> S·9H <sub>2</sub> O	8.3	65.2	18.6	<0.1	7.9
chrysocolla+CH <sub>6</sub> N <sub>2</sub> O <sub>2</sub> +Na <sub>2</sub> S·9H <sub>2</sub> O	5.2	69.1	18.6	0.9	6.1

Fig. 3. XPS comprehensive full spectrum of chrysocolla under various conditions (a) chrysocolla, (b) chrysocolla + Na<sub>2</sub>S·9H<sub>2</sub>O, (c) chrysocolla + CH<sub>6</sub>N<sub>2</sub>O<sub>2</sub> + Na<sub>2</sub>S·9H<sub>2</sub>OFig. 4. XPS (O1s) for a) chrysocolla, (b) chrysocolla + Na<sub>2</sub>S·9H<sub>2</sub>O, (c) chrysocolla + CH<sub>6</sub>N<sub>2</sub>O<sub>2</sub>+Na<sub>2</sub>S·9H<sub>2</sub>O

### 3.3. Zeta potential analysis

The relative motion of the mineral particles in the solution can be considered as an evidence reflecting the change of particles on the surface. It is helpful for studying the relationship between the Zeta

potential of the mineral surface and its adsorption properties in the exploration of chemical processes and the exchange law of mineral surfaces (Tchistiakov, 2000). This can be used to evaluate the interactions between flotation reagents and the mineral surface. The ion concentration, type, and state in the pulp solution affect the Zeta potential of minerals. The Zeta potential of minerals will also change depending on the ion type and ion concentration in the solution.

Fig. 7 shows the Zeta potential change before and after the addition of reagents. It can be seen that the Zeta potential had little change after adding  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  for  $\text{pH} > 7$ , while that after adding  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  and  $\text{CH}_6\text{N}_2\text{O}_2$  became higher than the pure chrysocolla samples. This may be due to the fact that  $\text{CH}_6\text{N}_2\text{O}_2$  can result in dissolving the surface of chrysocolla particles by reacting with Cu. Furthermore, the complex produced in the reaction can make the adsorption more stable, and enhance the activity of Cu on the chrysocolla surface. The flotation experiments led to the same results.

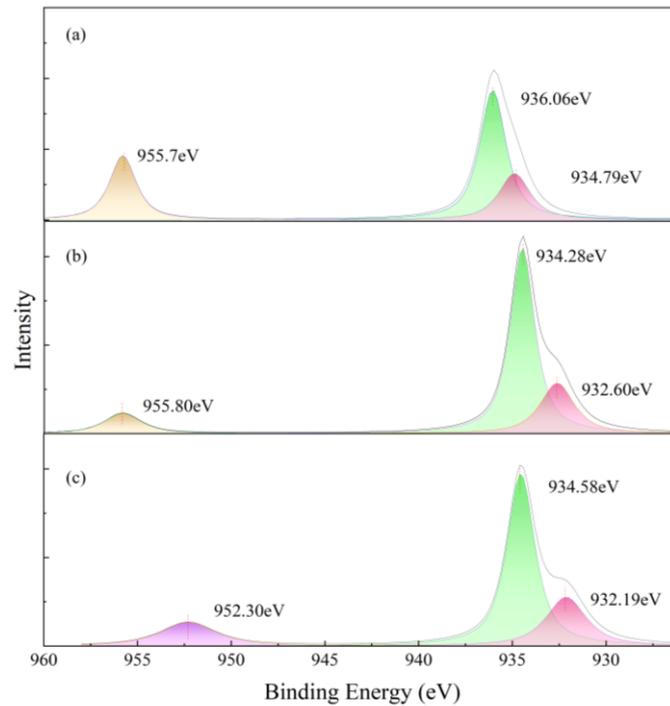


Fig. 5. XPS (Cu2p) for a) chrysocolla, (b) chrysocolla +  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , (c) chrysocolla +  $\text{CH}_6\text{N}_2\text{O}_2 + \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$

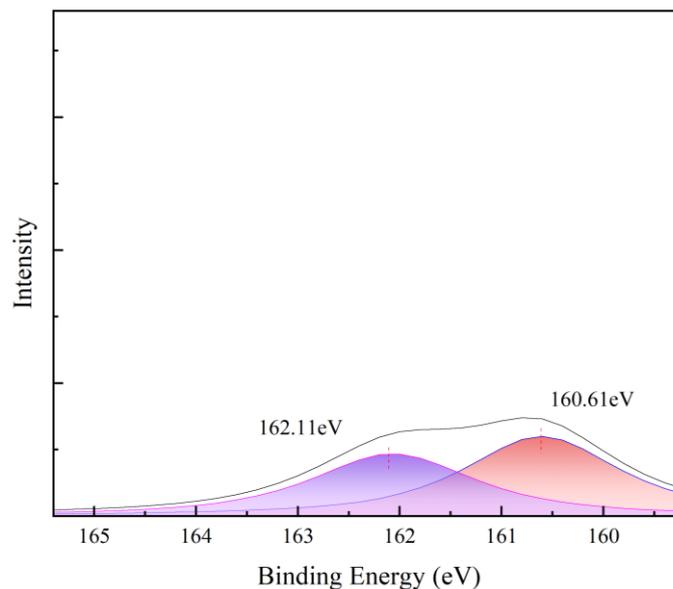


Fig. 6. XPS (S2p) for chrysocolla +  $\text{CH}_6\text{N}_2\text{O}_2 + \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$

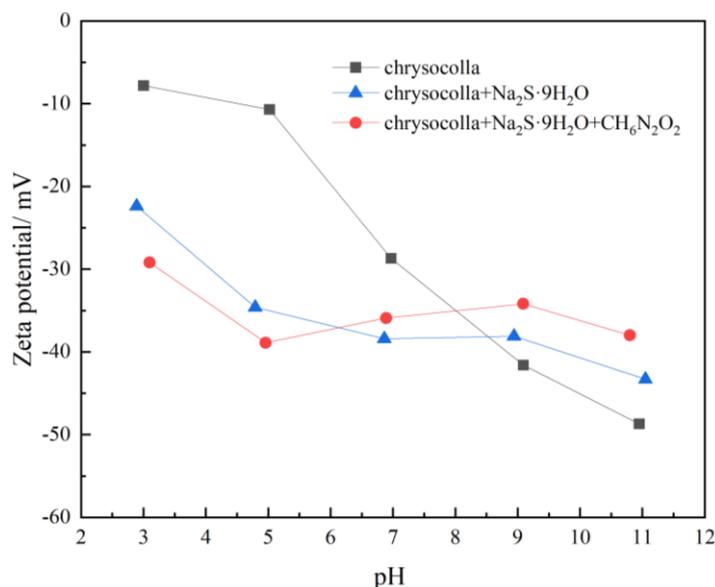


Fig. 7. Zeta potential of chrysocolla under the action of different reagents as a function of pH

### 3.4. AFM analysis

The two-dimensional geometrical topography, three-dimensional height topography, and cross-section height of AFM can indicate changes in the mineral surface height, under various flotation reagent conditions. Therefore, AFM is usually used to characterize the adsorption strength of reagents on the mineral surface.

The height morphology of the chrysocolla surface, before and after sulfidation, was observed in AFM images (two-dimensional (2D) and three-dimensional (3D)), as shown in Figs. 8(a), (b), and (c). In the latter, sample (a) was chrysocolla + DI water, sample (b) was chrysocolla + Na<sub>2</sub>S·9H<sub>2</sub>O (5×10<sup>-3</sup> mol/L), and sample (c) was chrysocolla + CH<sub>6</sub>N<sub>2</sub>O<sub>2</sub> (8×10<sup>-3</sup> mol/L) + Na<sub>2</sub>S·9H<sub>2</sub>O (5×10<sup>-3</sup> mol/L). The treatment time for all these reagents was 30 min. The cross-sectional height plot was generated by the NanoScope Analysis software (Bruker AXS, GmbH). The commonly used parameters for characterizing the roughness, that are the surface average roughness (Ra), maximum height roughness (Rmax), and root mean square roughness (Rq), were used to reveal the variation of the morphology and the height of mineral surfaces with the addition of the flotation reagent.

The cross-sectional height plot showed relatively uniform height, which indicates that the mineral particles were uniform and the surface was smooth, as shown in Fig. 9(b). This proved that the morphology image is suitable for the illustration of the sulfidation reaction strength. In addition, the height value of the peak ranged between -3 μm and 9 μm.

It can be observed from Figs. 8(a), (b), and (c) that the height value of the peak increased to 24.7 μm, and the minimum height is -5 μm. Furthermore, the surface was rougher than that of pure minerals. It can be seen from Figs. 8(a), (b), and (c) that the number of peaks is significantly less after adding CH<sub>6</sub>N<sub>2</sub>O<sub>2</sub>, the height value of the peak illustrated in the cross-sectional height plot was clearly increased to 49.5 μm, and the minimum height is almost -10 μm. The surface became rougher than that of direct sulfidation. This indicates that the sulfidation reaction is more active with the addition of CH<sub>6</sub>N<sub>2</sub>O<sub>2</sub>. This conclusion is consistent with the flotation studies.

### 3.5. SEM-EDS analysis

Fig. 9 shows the direct sulfidation and complex sulfidation of chrysocolla SEM images. Fig. 10 shows the direct sulfidation and complex sulfidation of chrysocolla EDS spectra. The results showed that after sulfidation without CH<sub>6</sub>N<sub>2</sub>O<sub>2</sub> (direct sulfidation), chrysocolla mainly consisted of 10.4% C, 31.2% O, 26.3% Si, and 32.1% Cu. After sulfidation with the addition of CH<sub>6</sub>N<sub>2</sub>O<sub>2</sub> (complex sulfidation), chrysocolla was mainly composed of 8.7% C, 34.7% O, 22.4% Si, 1% S, and 33.2% Cu. It can be seen that after adding CH<sub>6</sub>N<sub>2</sub>O<sub>2</sub> during sulfidation, the S content of chrysocolla increased by 1.04%. This

shows that after adding  $\text{CH}_6\text{N}_2\text{O}_2$ , the surface of chrysocolla was better combined with  $\text{S}^{2-}$ , and therefore more  $\text{CuS}$  was formed on the chrysocolla surface, which enhanced its sulfidation, and promoted the subsequent adsorption of xanthate on the mineral surface.

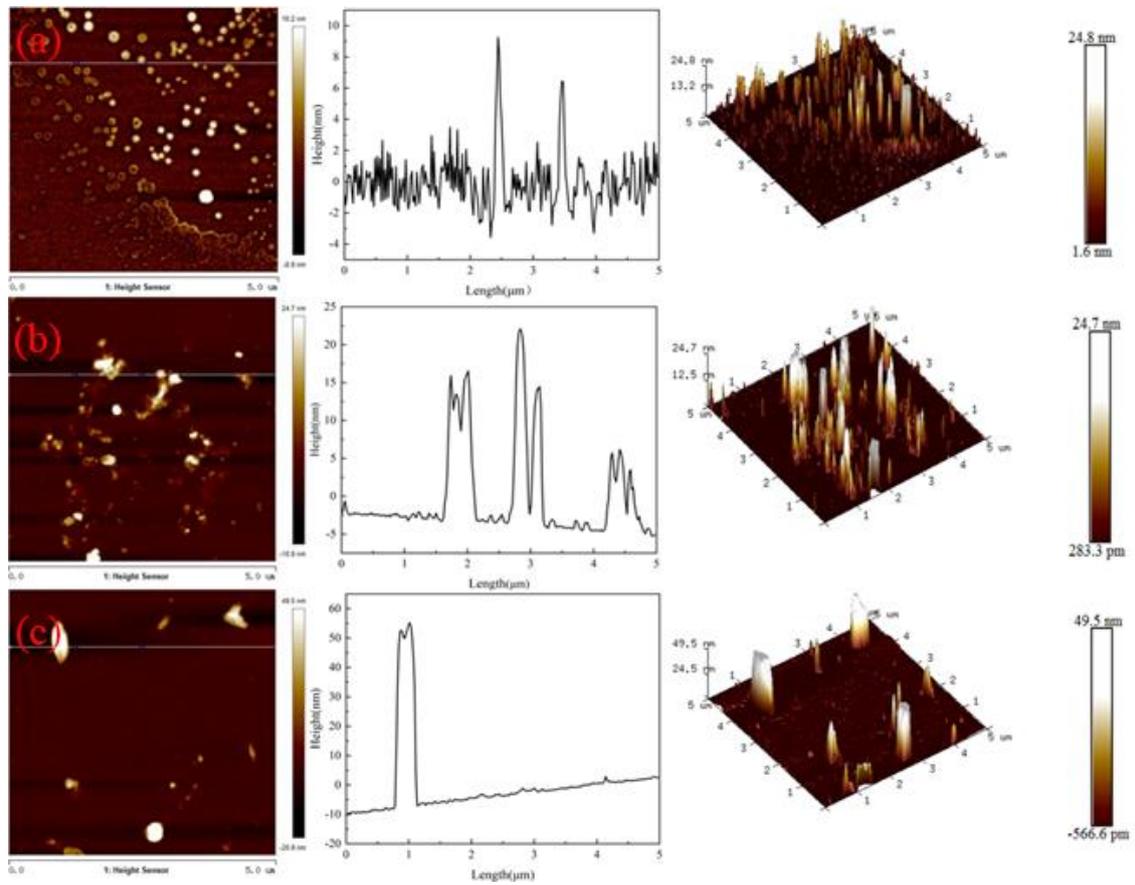


Fig. 8. AFM images after treatment with different reagents on the surface of chrysocolla: (a) chrysocolla + DI water, (b) chrysocolla +  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  ( $5 \times 10^{-3}$  mol/L), (c) chrysocolla +  $\text{CH}_6\text{N}_2\text{O}_2$  ( $8 \times 10^{-3}$  mol/L) +  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  ( $5 \times 10^{-3}$  mol/L)

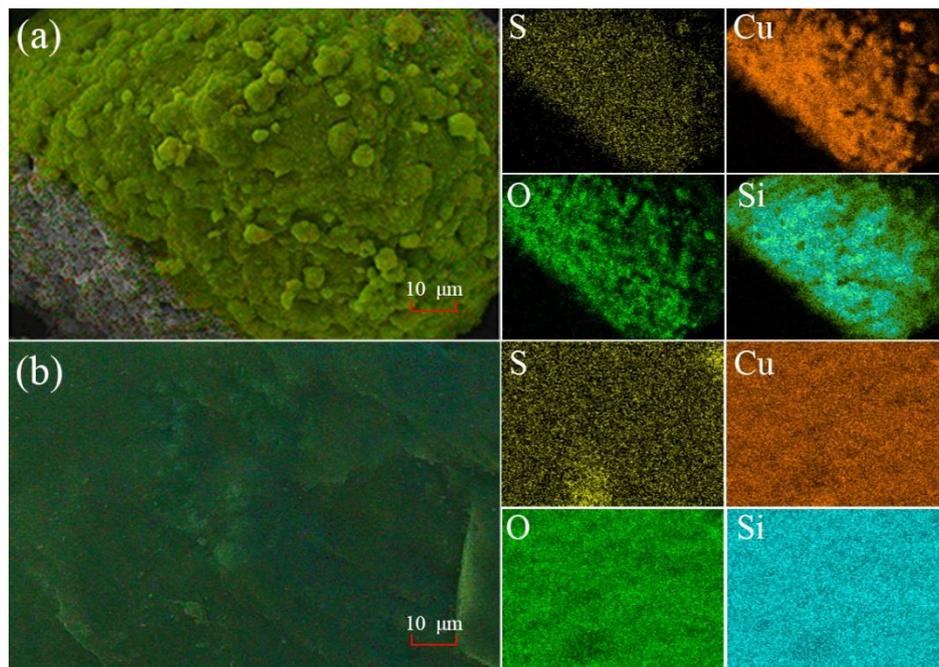


Fig. 9. SEM of the samples of the chrysocolla: (a) direct sulfidation, (b) complex sulfidation

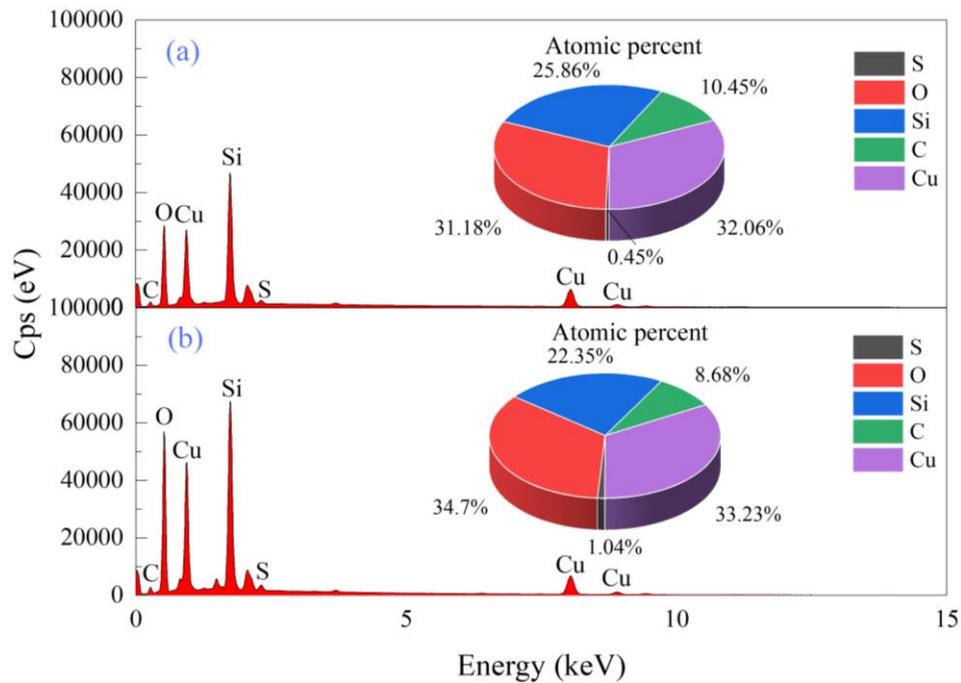


Fig. 10. EDS of the samples of the chrysocolla: (a) direct sulfidation, (b) complex sulfidation

### 3.6. Contact angle analysis

The wettability denotes the tendency of a phase in a multiphase fluid to spread or adhere to a solid surface. In flotation operations, it mainly involves three phases: gas, solid, and liquid. The wettability of minerals directly affects their floatability. The contact angle is defined as the angle  $\theta$  formed by the tangent of the gas-liquid interface at the intersection of the three phases: gas, liquid, and solid. It can express the degree of wettability. If  $\theta > 90^\circ$ , the solid surface is hydrophobic, which indicates that the liquid is not easily wetted by the solid, and the floatability is better. Fig. 11 shows the profile images in contact angle analysis, and Table 3 shows the measurement result. The angle values marked in Fig. 11 actually are the average results of contact angle on both sides. It can be seen from Table 3 that the contact angle of chrysocolla surface without reagents is  $62.9^\circ$ , which indicates a poor natural floatability and thus confirms the difficulty of flotation. When ammonium carbamate is added, the contact angle on the mineral surface increases to  $90.4^\circ$ , while the contact angles on the mineral surface while adding NaIX and NaIX +  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  are  $73.9^\circ$  and  $84.9^\circ$ , respectively. The results prove that the enhanced sulfidation significantly increases the hydrophobicity and floatability of the chrysocolla surface, which is consistent with the flotation test results.

Table 3. Surface contact angle of chrysocolla

Element	Surface contact angle
chrysocolla	62.9
chrysocolla+NaIX	73.9
chrysocolla+ $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ +NaIX	84.9
chrysocolla+ $\text{CH}_6\text{N}_2\text{O}_2$ + $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ +NaIX	90.4

### 3.7. Discussion

After  $\text{CH}_6\text{N}_2\text{O}_2$  dissolves in water, the following reaction occurs:



The ionization equations of  $\text{NH}_4\text{HCO}_3$  and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  are given by:



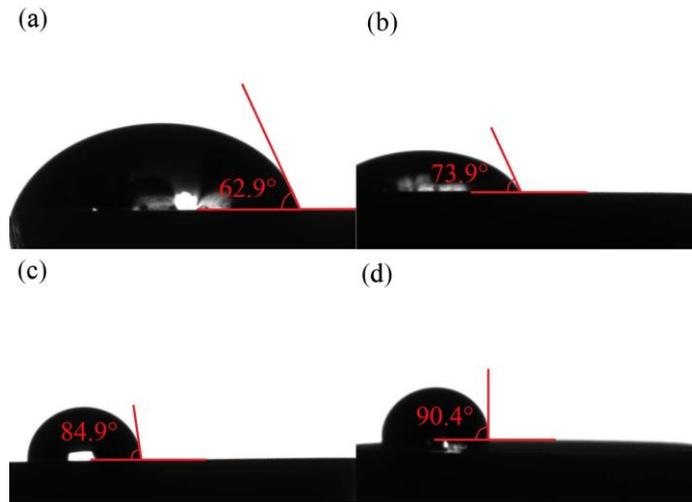
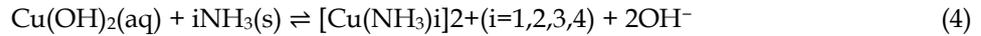


Fig. 11. The contact Angle of chrysocolla surface (a) chrysocolla, (b) chrysocolla + NaIX, (c) chrysocolla +  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  + NaIX, (d) chrysocolla +  $\text{CH}_6\text{N}_2\text{O}_2$  +  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  + NaIX

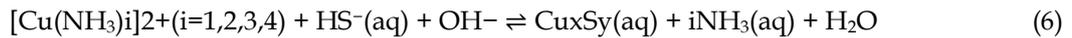
Fig. 12 shows the influence of the pH on  $\text{Cu}^{2+}$  and  $\text{NH}_4^+$  species in the solution. Copper species in the solution include six forms:  $\text{Cu}^{2+}$ ,  $\text{Cu}(\text{OH})_2(\text{aq})$ ,  $\text{Cu}(\text{OH})_3^-$ ,  $\text{Cu}(\text{OH})_4^{2-}$ ,  $\text{Cu}(\text{OH})^+$ , and  $\text{Cu}_2(\text{OH})_3^+$ . It can be seen that  $\text{Cu}(\text{OH})_2(\text{aq})$  is the dominant species when  $\text{pH} = 8-11$ . In addition, there are 4 forms of copper ammonium complexes:  $\text{Cu}(\text{NH}_3)^{2+}$ ,  $\text{Cu}(\text{NH}_3)_2^{2+}$ ,  $\text{Cu}(\text{NH}_3)_3^{2+}$ , and  $\text{Cu}(\text{NH}_3)_4^{2+}$ . It can also be observed that  $\text{Cu}(\text{NH}_3)^{2+}$  is the dominant species for  $\text{pH} = 8-11$ . Finally, it can be deduced that  $\text{NH}_4^+$  and  $\text{Cu}(\text{OH})_2$  can form a stable complex through a complexation reaction. The following reaction may occur in an aqueous solution:



The dissolution equilibrium of  $\text{Na}_2\text{S}$  in the solution is given by:



It can be seen from Fig. 13 that  $\text{HS}^-$  is the sulfur dominant species when the pH range is 8-11. Furthermore,  $\text{CuS}$  and  $\text{Cu}_2\text{S}_3^-$  were produced in the solution under the same pH, and the ion concentration of  $\text{CuS}$  is higher than that of  $\text{Cu}_2\text{S}_3^-$ . The reaction of the complex with  $\text{S}^{2-}$  is given by:



These reactions can explain how the  $\text{CuS}$  complex is produced. In addition, the whole process is consistent with the results of the mentioned analysis. For example, the XPS analysis proves the existence of  $\text{Cu}_x\text{S}_y$ .

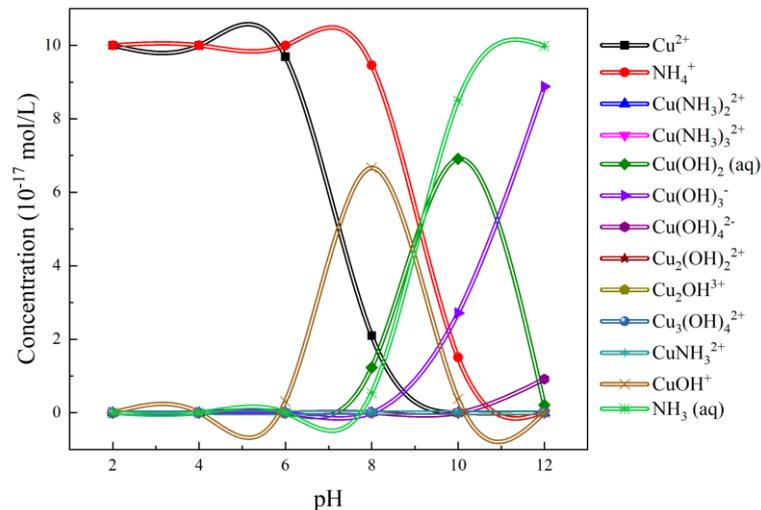


Fig. 12. Component distribution of  $\text{Cu}^{2+}$  and  $\text{NH}_4^+$  in solution system as a function of pH

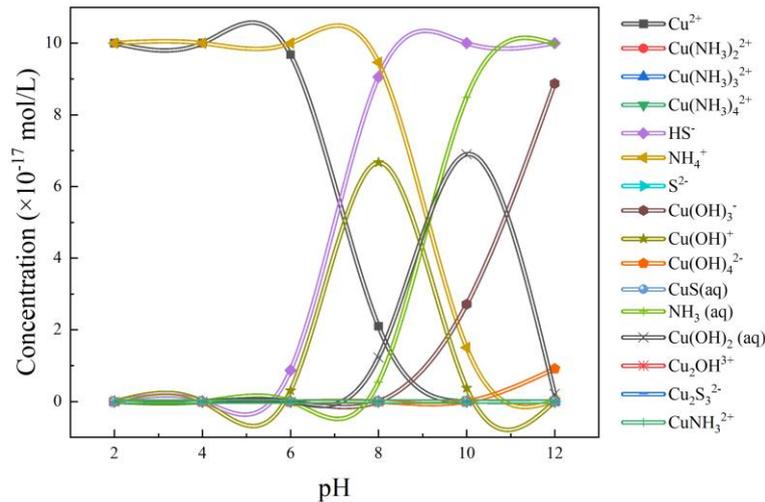


Fig. 13. Component distribution of  $\text{Cu}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{S}^{2-}$  in solution system as a function of pH

Fig. 14 shows the graphical abstract of the action between  $\text{CH}_6\text{N}_2\text{O}_2$  and chrysocolla. It can be seen in the diagram that  $\text{CH}_6\text{N}_2\text{O}_2$  has a catalysis in sulfidation of chrysocolla by circulating as a complexing agent. The Cu-S complex produced in the reaction can form a film in the surface of chrysocolla, which can improve the floatability of minerals.

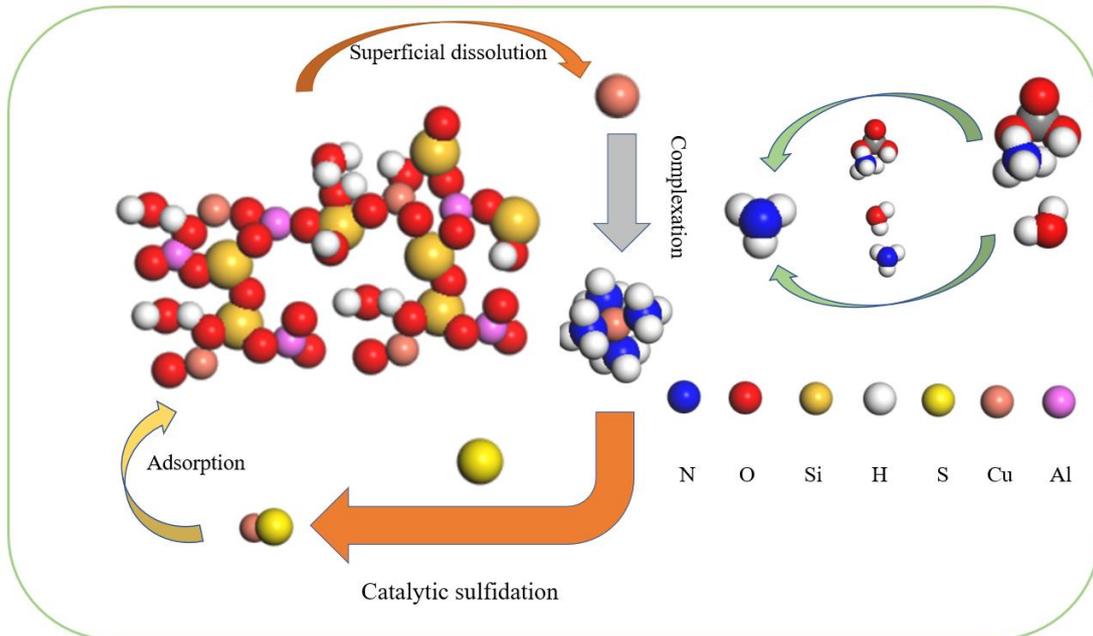


Fig. 14. Schematic diagram of surface modification of chrysocolla by ammonium carbamate and its response to flotation mechanism

#### 4. Conclusions

This paper studied the effect of  $\text{CH}_6\text{N}_2\text{O}_2$  as a complexing agent on the sulfide flotation of chrysocolla. In the process of sulfidation-xanthate flotation,  $\text{CH}_6\text{N}_2\text{O}_2$  reacted as a complexing agent with Cu to increase the activity of Cu on the chrysocolla surface. More complex CuS was produced and the efficiency was increased after adding  $\text{Na}_2\text{S}$ . Flotation experiments, Zeta potential, and XPS were used to study the impact of  $\text{CH}_6\text{N}_2\text{O}_2$  as a complexing agent on the sulfide flotation of chrysocolla. It can be seen in the flotation studies that the recovery of chrysocolla clearly increased 34.66% when adding  $\text{CH}_6\text{N}_2\text{O}_2$ . In the Zeta potential analysis, the Zeta potential of the chrysocolla surface after adding  $\text{CH}_6\text{N}_2\text{O}_2$  was significantly higher than that without  $\text{CH}_6\text{N}_2\text{O}_2$  for  $\text{pH} > 7$ . This may be due to the fact

that  $\text{CH}_6\text{N}_2\text{O}_2$  partially dissolved the chrysocolla surface and complexed with and stably adsorbed Cu, which enhanced the activity of Cu on the surface of  $\text{CH}_6\text{N}_2\text{O}_2$ . It can be deduced from the results of AFM analysis that the addition of  $\text{CH}_6\text{N}_2\text{O}_2$  promoted the adsorption of  $\text{Na}_2\text{S}$  on the chrysocolla surface, which led to an increase of the peak height by 24.8  $\mu\text{m}$ , compared with direct sulfidation. This strengthened the sulfidation effect on the surface and improved the flotation recovery. It can be observed from the SEM-EDS analysis that after adding  $\text{CH}_6\text{N}_2\text{O}_2$ , the chrysocolla surface better combined with  $\text{S}^{2-}$ , and the atomic concentration of S increased by 0.59%, thus forming more  $\text{CuS}$  species, which had a positive impact on sulfidation and flotation. The measurements of the contact angle indicated that the addition of ammonium carbamate improved the floatability of chrysocolla in sulfidation-xanthate flotation. More precisely, it led to the increase of the contact angle from 62.9° to 90.4°. This paper also detailed the whole reaction process of enhanced sulfidation, in which  $\text{CH}_6\text{N}_2\text{O}_2$  is considered to perform a catalytic action.

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