Selective Flotation of Copper Oxide Minerals with A Novel Amino-Triazole-Thione Surfactant: A Comparison to Hydroxamic Acid Collector

Jun Liu, Zhe Hu, Guangyi Liu, Yaoguo Huang, and Zhiyong Zhang

College of Chemistry and Chemical Engineering, Central South University, Changsha, China

ABSTRACT
Developing specific flotation collectors to improve the separation and enrichment of copper oxide minerals from their ores is still a challenging job. In this article, a novel chelating collector, 5-(2,4,4-trimethylpentyl)-4-amino-1,2,4-triazolidine-3-thione (TMATT), was designed to separate and recover copper oxide minerals, and its flotation response to malachite, calcite, and quartz was compared with that of the traditional collector n-octyl hydroxamic acid (OHA). The findings of contact angle and micro-flotation indicated that TMATT exhibited stronger hydrophobization and better flotation performances to malachite than OHA, and also held the high flotation selectivity against quartz and calcite. The bench-scale flotation outcomes showed that TMATT achieved the high-efficient flotation separation and enrichment of copper oxide minerals from the mixed sulfide-oxide copper ore. XPS, FTIR, AFM, and zeta potential deduced that the adsorption of malachite toward TMATT was related to the reduction of surface Cu(II) to Cu(I) and the formation of TMATT-Cu(I) surface complexes in which the exocyclic N and S atoms of TMATT bonded with the surface Cu(I) on malachite. The superior hydrophobicity of TMATT-Cu(I) surface complexes in comparison to that of OHA-Cu(II) surface complexes, the favorable five-membered ring bonding mode on malachite surfaces and the preferable chelating selectivity to soft acid Cu(I) rather than to hard acid Ca(II), deserved TMATT to possess better flotation response to malachite against calcite than OHA.

1. Introduction
As an important non-ferrous metal, copper is widely used in the fields of daily necessities, industries, and national defenses. The significant raw materials for copper production are of copper sulfide and oxide minerals. With the rapid and continuous exploitation of copper sulfide ores, copper oxide or mixed oxide-sulfide copper ores have become indispensable in compensation of copper shortage (Hayes et al. 1987; Wang and Xie 1990; Deng and Chen 1991; Cheng and Iwasaki 1992; Ecrola and Paloaari 1995; Abramov and Forsberg 2005; Alim 2007; Celik et al. 2010; Bakalarz et al. 2015; Hassanzadeh et al. 2017; Hassanzadeh and Karakaş 2017; Wu et al. 2017; Bahrami et al. 2018; Katwika et al. 2019). Besides the leaching, solvent extraction and electro-winning (LSE-EW) technique (Bartos 2002; Kordosky 2002), froth flotation is another commercial technology for separation and purification of copper oxide minerals from copper mines (Fuerstenau et al. 2007; Nagaraj and Farinato 2016).

To improve the surface hydrophobicity of oxide copper minerals is prerequisite for separation of them from gangue minerals by froth flotation. On this point, a collector plays a crucial role (Ahmed and Jameson 1989; Schulze 1989; Sreenivas and Manohar 2000; Fuerstenau et al. 2007; Gharai and Venugopal 2016; Nagaraj and Farinato 2016; Liu et al. 2017, 2018b). A flotation collector selectively adsorbs on to the surfaces of oxide copper minerals through its minerophilic groups, and then, its hydrophobic groups attach bubbles, thus oxide copper minerals achieve the selective hydrophobicity and enrichment.

The flotation collectors for CuO minerals included fatty acids (Bulatovic 2010), hydroxamic acids (Peterson et al. 1965; Lee et al. 1998; Hope et al. 2012a, 2012b), aldoximes (Ananthapadmanabhan and Somasundaran 1985), phosphonic acids (Li et al. 2015; Liu et al. 2018a), xanthates (Rao and Finch 2003), dithiophosphates (Booth et al. 1971), thioureas (He et al. 2016), mercaptobenzoxazole (MBO) (Yekeler et al. 2006b; Liu et al. 2012), mercaptobenzimidazole (MBI) (Liu et al. 2012), mercaptobenzothiazole (MBT) (Yekeler et al. 2006a), amino thiophenol (ATP) (Barbaro et al. 1997), and so on. Among them, xanthates are effective flotation collectors for the surface-sulfidized CuO minerals, and the presulfidization flotation with xanthates is a primary technology for separation and beneficiation of CuO minerals (Raghavan et al. 1984; Bulatovic 2010; Park et al. 2016), while the sulfidizing agents such as NH₄HS, NaHS or Na₂S are easy to decompose with processing time and their dose is hard to be precisely controlled (Park et al. 2016; Wu et al. 2017). Hydroxamic acids have been proved to be chelating collectors for CuO minerals (Peterson et al. 1965; Lee et al. 1998; Sreenivas and Manohar 2000; Hope et al. 2012a, 2012b), and

CONTACT
Guangyi Liu
lgy_2013@csu.edu.cn College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China

补数据 for this article can be accessed here.

© 2019 Taylor & Francis Group, LLC
the combination application of hydroxamates with xanthates would contribute to the flotation recovery of CuO minerals (Lee et al. 2009; Chen and Peng 2018). Nevertheless, hydroxamate collectors exhibit a certain affinity to iron/calcium-bearing minerals, leading to the low flotation selectivity for copper oxide minerals against iron/calcium minerals (Buckley et al. 2012; Marion et al. 2017). MBI, MBT, MBO or ATP possess strong chelating power to CuO minerals such as malachite \((\text{Cu}_2(\text{OH})_2\text{CO}_3)\), however, the inadequate hydrophobicity of their benzene ring restricts their application in froth flotation.

Amino-azole-thione chelators have the S, N-donor atoms connecting to the conjugative amino-azole-thione structure, and exhibit a powerful affinity to metal atoms (Eldakar and Nobe 1977; Clark et al. 1999; Kajdan et al. 2000; Yi et al. 2004; Liu et al. 2006, 2016a; Qu et al. 2016), especially to copper atoms (Clark et al. 1999; Kajdan et al. 2000; Yi et al. 2004; Qu et al. 2016; Liu et al. 2016a). Kajdan et al. (2000) thought that 5-ethyl-4-amino-1,2,4-triazole-3-thione reacted with Cu atoms to generate five-membered-ring complexes. Clark et al. (1999) found that 5-methyl-4-amino-1,2,4-triazole-3-thione coordinated with Cu atoms through its exocyclic N and S atoms. These coordination characteristics render amino-azole-thione chelators to be the effective corrosion inhibitors (Quraishi et al. 2002; Dandia et al. 2012; Chebabe et al. 2014). Chebabe et al. (2014) investigated that the anti-corrosion performances of 5-methyl-4-aminoo1,2,4-triazole-3-thione to bronze in 3% NaCl solutions. Dandia et al. (2012) considered that 5-alkyl-4-amino-1,2,4-triazole-3-thione homologues might be green corrosion inhibitors for copper in HCl solutions. Therefore, it might be interesting to understand the hydrophobic flotation and its mechanism of amino-azole-thione chelators to copper minerals.

In this article, 5-(2,4,4-trimethylpentyl)-4-amino-1,2,4-triazole-3-thione (TMATT) was first synthesized and characterized by NMR (nuclear magnetic resonance) and FTIR (Fourier transform infrared) spectra. Its collecting performance to copper oxide minerals such as malachite, chrysocolla, and cuprite. The iron-bearing minerals included pyrite and hematite. The non-sulfide gangue minerals contained dolomite, calcite, quartz, muscovite, and feldspar. The oxidation proportion of copper minerals in the samples was about 30.26% and malachite was the dominated copper oxide minerals. The XRF results of the ore samples were also presented in Supporting Information (Table S1).

2.2. Micro-flotation tests

Micro-flotation experiments were performed in the Hallimond tube according to the previous approach (Liu et al. 2018c). In each operation, 2g minerals (for the artificially mixed minerals tests, the weight proportion of malachite to calcite or quartz was 1:1) were put into a 500 mL beaker where a given amount of water, pH regulator (1 mol·L\(^{-1}\)) or 0.1 mol·L\(^{-1}\) HCl or NaOH solutions), collector (TMATT or OHA), methyl isobutyl carbinol (MIBC, \(1 \times 10^{-3} \text{ mol·L}^{-1}\)) and additional H\(_2\)O were added in succession to come to 220 mL. After stirring for 3 min at 25 ± 1°C, the suspension was transferred to the Hallimond tube and its pH value was recorded. Then, micro-flotation was implemented for 3 min via 200mL·min\(^{-1}\) N\(_2\). The flotation foam and underflow pulp were separately filtrated, dried, and weighed. The recovery was computed on the base of formulas as are same as Equation (1) for single mineral, Equation (2) for malachite and Equation (3) for calcite or quartz in the artificially mixed minerals, respectively.

\[
\varepsilon = \frac{m_1}{m_1 + m_2} \times 100\% \tag{1}
\]

\[
\varepsilon_{\text{Malachite}} = \frac{m_1 \times \beta_1}{m_1 \times \beta_1 + m_2 \times \beta_2} \times 100\% \tag{2}
\]

\[
\varepsilon_{\text{Calcite/Quartz}} = \frac{m_1 \times (1 - \beta_1)}{m_1 \times (1 - \beta_1) + m_2 \times (1 - \beta_2)} \times 100\% \tag{3}
\]

Where \(m\) is the mass and \(\beta\) is the copper grade, and 1 and 2 separately represent the foam and underflow products. The average recovery of three independent experiments was displayed.
2.3. Bench-scale flotation experiments

Bench-scale flotation experiments were carried out with the 3.0 dm³ XFD-63 flotation apparatus (Jilin Exploration Machinery, China). The flowsheet of the locked-cycle flotation experiment is displayed in Supporting Information (Figure S2), which was originated from the actual production process with SIBX (sodium isobutyl xanthate) as the only collector. 1.0 kg of ~2 mm real ores as well as 0.6 kg tap water were ground to 86% passing 76 μm in a ø240 × 90 mm XMQ stainless steel ball mill. Then, the slurry, extra tap water, 300 g/t NaSH, 80 g/t SIBX collector and 40 g/t MIBC frother were sequentially put into the XFD-63 flotation apparatus with about 1200 rpm agitation speed. After agitating the slurry for 3 min, air was introduced and the rougher flotation was conducted for 5 min during which the floated products (copper concentrates) were concentrated.

Afterwards, 800 g/t NaSH and a given amount of collectors were added in order and the slurry (underflow) was agitated for extra 3 min. Then, the scavenger flotation was implemented for 3 min. The collected scavenger concentrates (froth products) were returned to the next cycle used for the rougher flotation feed. The copper concentrates and tailings were successively filtered, dried, weighted, sampled, and assayed for copper.

2.4. AFM and contact angle measurements

The Dimension Icon AFM (Bruker, USA) was applied in imaging the morphology of malachite surface via the peakforce tapping in ScanAsyst mode. The JC2000C device (Zhongchen Digital, China) was adopted to determine the contact angle through the sessile drop method. The malachite slice was orderly wet-polished by hand with SiC paper and Al₂O₃ powder, and then cleaned by Milli-Q H₂O and dried by high-purity N₂ until its surface was very smooth under optical microscope. After immersing in 1 × 10⁻⁵ mol·L⁻¹ TMATT for 5min, the AFM images and contact angle of the malachite slice were measured.

To investigate the effect of pH or collector concentration on malachite wettability, the followed contact angle trials were carried out. The newly-polished malachite slice as well as 30 mL Milli-Q H₂O was put into a 100 mL beaker where a desired dose of pH regulator, TMATT or OHA solutions and extra H₂O were successively incorporated to reach 50 mL. After immersing 3 min, the malachite slice was taken out, dried by high-purity N₂. The prepared malachite chunk was loaded on the goniometer stage, and 10 μL Milli-Q water was loaded on its surface through an injection control device. After a period of 30s, a certain amount of Milli-Q water was took out. Another 30s later, the receding contact angle was measured. And the average value of three independent contact angle measurements was presented with a deviation below 1.5°.

2.5. Zeta potential measurements

The ZetaPALS analyzer of Brookhaven (USA) was applied during zeta potential measurements. 0.05 g mineral samples were added to 50 mL KCl solutions (0.01 mol·L⁻¹) with or without 4 × 10⁻⁵ mol·L⁻¹ TMATT. After regulating the suspension to a given pH via dilute KOH/HCl solutions, the zeta potential of mineral particles was independently measured for six times and their average value was presented with a variation less than ±6 mV.

2.6. XPS and FTIR spectra measurements

0.5 g malachite and 50 mL of 1 × 10⁻³ mol·L⁻¹ TMATT solutions (50% ethanol, v/v) were mixed in a 250mL flask. The mixture was oscillated for 3h at 25 ± 0.5. Then, malachite particles were centrifuged, rinsed several times with Milli-Q H₂O, dried in a vacuum oven.

After blending 1 × 10⁻³ mol·L⁻¹ TMATT solutions (50% ethanol, v/v, 100 mL) with 1 × 10⁻³ mol·L⁻¹ Cu²⁺ (50% ethanol, v/v, 100mL), the blue sediments appeared, then filtered, washed with Milli-Q H₂O and desiccated.

The TMATT-Cu²⁺ sediments, and malachite with or without TMATT modification were analyzed through FTIR and XPS. Thermo Scientific ESCALAB 250Xi (USA) was applied for XPS detection (Liu et al. 2016a). And Al Kα (hv = 1486.71eV) was used as the radiation source under 10⁻⁹ to 10⁻⁸ Torr. The XPS bands were fitted via Gaussian and Lorentzian functions and corrected by assigning the C 1s binding energy at 284.6eV.

3. Results and discussion

3.1. Synthesis and characterization of TMATT

The synthetic process of TMATT was presented in Scheme 1. Thiocarbonyldrazide (0.04 mol) and 3,5,5-trimethyhexanoic acid (0.12 mol) were stirred for 8 h under 135°C. Then, the mixture was cooled and a white sediment emerged. After being filtrated, washed with Milli-Q H₂O, the precipitates were recrystallized from ethanol-water solutions to obtain a white tabular crystal TMATT (yield: 73.34%, m.p.198.6–199.4°C).

TMATT characterization:¹H-NMR (DMSO-d₆, 400MHz; d = doublet, t = triplet, s = singlet, and m = multiplet): δ ppm 13.433 (s, 1H NH/SH); 5.542 (s, 2H, NH); 2.300–1.111 (m, 2H, CH₂); 2.633–1.999 (m, 1H, CH); 0.917–0.903 (m, 3H, CH₃); 1.288–1.111 (m, 2H, CH₂); 0.855 (s, 9H, CH₃); 13C-NMR (DMSO-d₆, 400MHz): δ ppm 166.179, 151.815, 50.390, 33.904, 31.259, 30.098, 27.302, 22.893.

3.2. Contact angle

The receding contact angle of malachite surfaces modified by TMATT or OHA as a function of pH or their concentration is shown in Figure 1. After TMATT or OHA modification, the hydrophobicity of malachite surfaces increased. Figure 1a demonstrates that at pH 6.5–10.5 and 2.5 × 10⁻⁵ mol·L⁻¹ collector concentration, TMATT returned bigger receding contact angle of malachite than that of OHA. And the favorable pH for improving malachite hydrophobicity appeared at pH ~9.5 where the receding contact angle of malachite reached 65.5 ± 1.1° for TMATT or 57.2 ± 1.2° for OHA. Figure 1b exhibits that
at pH ~9.5, the receding contact angle of malachite increased with raising collector dose from $0.5 \times 10^{-5}$ to $1.5 \times 10^{-5}$ mol·L$^{-1}$, and over $1.5 \times 10^{-5}$ mol·L$^{-1}$ TMATT or OHA, the increase of receding contact angles was very slow.

3.3. Micro-flotation results

3.3.1. Flotation of single minerals

The flotation recovery as a variable of pH (at $2.5 \times 10^{-5}$ mol·L$^{-1}$ TMATT or OHA) or collector dose (at pH ~7.5) is shown in Figure 2. It displayed that in comparison to OHA, TMATT owned superior flotation selectivity against calcite and quartz, and excellent flotation affinity toward malachite which agreed with the contact angle findings. As shown in Figures 2a–c, using TMATT as a collector, malachite flotation recovery reached 73% at pH ~6.5, and increased sharply to 93% under pH ~7.5, and then maintained at high level at pH 7.5–10.5. As for OHA, malachite flotation recovery lifted dramatically with increase of pulp pH from 6.5 to 8.5, and then lifted tardily with pH change from 8.5 to 10.5. For calcite and quartz, low pH values (pH ≤ 7.5) were unsuitable for their flotation enrichment by using TMATT or OHA as a collector.

Figure 2b–d displays that at pH ~7.5, malachite particles were floated out over 81% or 93% by using $0.5 \times 10^{-5}$ or $2.5 \times 10^{-5}$ mol·L$^{-1}$ TMATT, while only around 55% or 80% with $0.5 \times 10^{-5}$ or $2.5 \times 10^{-5}$ mol·L$^{-1}$ OHA. When collector concentration was below $2.5 \times 10^{-5}$ mol·L$^{-1}$, OHA recovered less than 55% calcite or 30% quartz, while TMATT only floated out less than 39% calcite or 20% quartz particles.

3.3.2. Flotation of artificially mixed minerals samples

To further assess TMATT’s flotation properties, the flotation experiments for the mixed minerals samples (the weight ratio of malachite to calcite or quartz was given to 1:1) were implemented and the findings are shown in Figure 3. Figure 3a–c exhibits that TMATT effectively separated malachite from its mixture with calcite or quartz under pH 7.5–10.5. Compared with the results of the single mineral flotation as presented in Figure 2a–c, malachite in the artificially mixed minerals samples kept excellent floatability under pH 7.5–10.5, while the flotation recoveries of calcite significantly decreased and those of quartz slightly increased, which might respectively owe to the competitive adsorption between malachite and calcite, and the flotation entrainment of malachite to quartz. In addition, Figure 3 indicates that compared to OHA, TMATT recovered more malachite particles and less calcite or quartz particles from their respective mixture, inferring that TMATT held better flotation selectivity to malachite against calcite and quartz than OHA, which was identical to the findings of the single mineral flotation tests. The findings of artificially mixed minerals flotation offered additional evidences that TMATT possessed excellent flotation affinity toward malachite and high flotation selectivity against calcite and quartz.

3.4. Bench-scale flotation results

The outcomes of the locked-cycle flotation experiments are shown in Table 1. It displayed that under the operation conditions (see Figure S2), the TMATT + SIBX system achieved the copper concentrates with 23.16% Cu grade and 88.65% Cu recovery, and for the OHA + SIBX system, the Cu grade and recovery in the copper concentrates were 20.82% and 81.74%, respectively. In comparison to the single SIBX system, the TMATT + SIBX combination obtained higher flotation separation efficiency to increase the Cu recovery and grade by 10.04% and 0.73%, while for the OHA + SIBX combination, the Cu recovery lifted by 3.13% and the Cu grade reduced by 1.61%, respectively. Therefore, TMATT possessed an excellent flotation affinity toward copper minerals and selectivity against gangue minerals including dolomite, calcite, quartz, et al.. For the most of copper sulfide minerals was floated out by SIBX collector during the rougher flotation.
operation, the copper minerals enriched by the scavenger flotation were dominated by copper oxide minerals such as malachite, i.e., TMATT was a special collector for flotation separation and enrichment of CuO minerals, which coincided with the micro-flotation outcomes.

3.5. AFM results
The AFM images of malachite surfaces are listed in Figure 4. It exhibited that the root-mean-square (rms) roughness for the freshly-polished malachite surfaces was 0.277 nm and the scratches produced by polishing could be clearly seen. After
TMATT treatment of 5 min, the rms roughness of malachite surfaces increased to 0.569 nm as indicated in Figure 4b, the foregoing scratches from polishing almost vanished and the aggregates covered the whole malachite surfaces with the significantly increasing receding contact angle, which inferred that TMATT molecules adsorbed on malachite surfaces.

3.6. Zeta potential results

The relationship of malachite’s zeta potential with pH is exhibited in Figure 5. It displayed that the isoelectric point (IEP) for malachite powders occurred on pH ~8.3, adjacent to the previous value of pH ~8.8 (Choi et al. 2016). In the presence of 4 × 10⁻⁵ mol·L⁻¹ TMATT, malachite’s zeta potential became more negative and its IEP shifted to lower pH value at ~6.9, which recommended that TMATT might attach on the positively charged sites of copper atoms on malachite surfaces.

3.7. FTIR spectra results

The FTIR spectra of TMATT, TMATT-Cu²⁺ sediments, and malachite with or without TMATT modification are displayed in Figure 6 and Table 2. They demonstrated that the NH and NH₂ adsorption bands of TMATT emerged at ~3253, 3157, 3041, and 1633 cm⁻¹. After interaction with Cu²⁺, the NH₂ bands appeared at ~3317, 3188, and 1630 cm⁻¹, while the NH peaks almost vanished on the TMATT-Cu²⁺ sediments. Additionally, the S-H stretching vibrations at ~2756 cm⁻¹ for TMATT also disappeared on the TMATT-Cu²⁺ sediments. The change of N-H and S-H adsorption bands implied that TMATT’s N-NH-(= S)-N(NH₂) group rearranged to the N-N = C(-SH)-N(NH₂) configuration which reacted with cupric ion to generate Cu-S bond, delivering the H ion into solutions. Furthermore, the N-NH-(= S)-N(NH₂) complex vibrations at ~1566 and 1480 cm⁻¹ for TMATT respectively shifted to lower frequencies at ~1529 and 1469 cm⁻¹ in TMATT-Cu²⁺ sediments, inferring an increasing electron density of N-N = C(-SCu)-N(NH₂) group, which suggested an extra bonding action of copper with the exocyclic N atom of TMATT (Qu et al. 2016; Liu et al. 2016a, 2016b). The C-S peaks moved to lower frequency at ~1032 cm⁻¹ in the TMATT-Cu²⁺ sediments, further recommending the generation of Cu-S bond (Qu et al. 2016; Liu et al. 2016a, 2016b). The peaks at <758 cm⁻¹ in TMATT spectrum (a) disappeared in TMATT-Cu²⁺ spectra (b), might due to the trizole ring deformation. Figure 6c–d exhibits that after TMATT modification, the C-H IR peaks at ~2953 cm⁻¹ occurred on malachite surfaces, deducing the adsorption of TMATT on malachite.

3.8. XPS results

3.8.1. Survey XPS

Figure 7 displays the XPS survey spectra of malachite with or without TMATT modification, and Table 3 lists the atomic concentration of elements. They showed that after TMATT cover, the atomic proportion of N, S, and C atoms increased and that of Cu and O decreased, giving a distinct evidence of TMATT adsorption on malachite surfaces. And the atomic proportion of N to S was near to 4:1, which was identical with that in the TMATT molecule.

3.8.2. XPS high-resolution spectra

The XPS high-resolution spectra of TMATT, TMATT-Cu²⁺ sediments and malachite with or without TMATT cover are displayed in Figure 8 and Table 4.

Figure 8(I) and Table 4 exhibit that the Cu 2p₃/₂ XPS of the TMATT-Cu²⁺ sediments occurred at ~932.24 eV, which was derived from Cu(I) sulfide (Hope et al. 2010; He et al. 2016), indicating the formation of TMATT-Cu(I) complexes via reducing Cu(I) to Cu(I) by TMATT. The Cu 2p₃/₂ XPS peak of

![Figure 4. AFM topographic images (1×1 µm²) of malachite surfaces as well as the corresponding contact angles (a) freshly-polished surfaces (R_q = 0.277 nm) and (b) TMATT treatment of 5min (R_q = 0.569 nm).](image-url)
Malachite was observed at ~934.68 eV, owning to Cu(II) oxides (Yoshida et al. 1979). After TMATT modification of malachite, two Cu 2p3/2 XPS bands at ~932.34 and 934.79 eV appeared, deducing the generation of TMATT-Cu(I) surface complexes on malachite through reducing surface Cu(II) by TMATT. Meanwhile, the copper atoms in the inner layers of malachite remained the characteristics of Cu(II) oxides.

Figure 8(2) and Table 4 display that the S 2p3/2 XPS of TMATT, TMATT-Cu2+ sediments and malachite modified by TMATT separately emerged at ~162.26, 162.54 and 162.46 eV, which was related to the sulfur atom of C = S, Cu-S and Cu-S groups (Yoshida et al. 1979; Hope et al. 2010). This inferred that after interaction with Cu2+ or malachite, the thione S atom of TMATT was changed into the thiolate S atom of TMATT-Cu complexes. The increased binding energy inferred an electron-donating effect of the S atom to the Cu atom.

Figure 8(3) and Table 4 exhibit that the N 1s XPS adsorption bands of TMATT were split into two ingredients at ~400.28 and 401.36 eV with near 1:1 atomic proportion, being respectively attributed to the N atoms of C-NH-N = C and C-N(-NH2)-C configurations (Qu et al. 2016; Liu et al. 2016a, 2016b). After reaction with Cu2+ or malachite, the XPS bands of N 1s were consisted of three components respectively at ~399.26, 400.43, and 401.22 eV, with corresponding atomic ratio close to 2:1:1. The lowest XPS bands at ~399.26 eV were attributed to the Na atom in C=N-N=C group (Qu et al. 2016; Liu et al. 2016a, 2016b), the reduced binding energy meant the increased electron density in the C = N-N = C group, which agreed with

| Table 2. The characteristic IR adsorption bands of TMATT and TMATT-Cu2+ sediments. |
|---------------------------------------------|
| TMATT/cm⁻¹ | TMATT-Cu²⁺ precipitates/cm⁻¹ | Assignments |
| 3253, 3157, 3041 (Smičius et al. 2007; Nath et al. 2008) | 3317, 3188 | NH₂, NH |
| 2953, 2899, 2868 (Hipler, Fischer, and Müller 2002) | 2953, 2906, 2868 | C-H |
| 2756 (Chufán, Pedregosa, and Borrás 1997) | 1630 | S-H |
| 1633 (Smičius et al. 2007) | 1529 | C≡N |
| 1566 (Smičius et al. 2007) | 1469 | N=C(=S)-N=N |
| 1480 (Liu et al. 2016a) | - | C≡S |
| 1040 (Hipler, Fischer, and Müller 2002) | 1032 | C-S-Cu |
the FTIR blue shift as presented in Figure 8 and Table 3. The XPS bands at ~400.43 eV were probably due to the N atom in the Cu-NH$_2$ group (Qu et al. 2016; Liu et al. 2016a, 2016b) and the decreased binding energy implied the electron-back-donation effect of the Cu atom to the N atom. The bonding interaction between Cu atom and the exocyclic N atom of 4-amino-1,2,4-triazole-3-thione compounds has been proved by the findings of X-ray single-crystal diffraction (Clark et al. 1999; Kajdan et al. 2000). The highest binding energy at ~401.22 eV might be owed to the N atom in the C-N-C group, which had an insignificant change in comparison with that in TMATT molecule.

The XPS outcomes and analyses deduced that TMATT chemisorbed on malachite surfaces to generate TMATT-Cu(I) surface complexes where the exocyclic N and S atoms of TMATT combined with surface Cu(I) atoms which were in situ produced by TMATT reduction of surface Cu(II) atoms.

### 3.9. Discussion

The results of contact angle and flotation displayed that TMATT exhibited stronger hydrophobization to malachite than OHA, and realized better flotation enrichment and separation of malachite against calcite and quartz.

The outcomes of XPS, FTIR, AFM, and zeta potential deduced that the exocyclic N and S atoms of TMATT bonded with Cu(I) atoms (which was in situ produced by TMATT reduction of Cu(II)) on malachite surfaces to generate TMATT-Cu(I) complexes (Qu et al. 2016; Liu et al. 2016a, 2016b). The recommended adsorption model of malachite to TMATT is presented in Figure 9a. For OHA, it has been reported that the hydroxamate group coordinated with surface Cu(II) atom to create the OHA-Cu(II) complexes (Farkas et al. 1998; Griffith et al. 2011). As seen from Figure 9, TMATT and OHA separately chemisorbed on malachite surfaces to form the five-membered ring structures. While, the TMATT-Cu(I) surface complexes might be more favorable to improving malachite floatability than the OHA-Cu(II) surface complexes, resulting in better flotation separation and enrichment of malachite by using TMATT collector.

The log P (P, partition coefficient, is defined as a proportion of the concentrations of a solute between n-octanol and water) is a measure of the hydrophobicity and hydrophilicity of a surfactant. The higher log P value means the better hydrophobicity. The log P values calculated by Chemoffice 2010 were 2.56 and 1.58 for TMATT and OHA, respectively, suggesting the stronger hydrophobization of TMATT to malachite than OHA.

OHA exhibits strong affinity to cupric atoms, and can form OHA-Cu(II) complexes on malachite surfaces (Farkas et al. 1998; Griffith et al. 2011). OHA can also react with Ca$^{2+}$ atoms and adsorb on calcite surfaces (Rai et al. 2002; Zhang et al. 2017). While Cu$^{2+}$ possesses stronger affinity toward OHA than Ca$^{2+}$ (Marion et al. 2017), which was the reason that OHA floated out more malachite than calcite as listed in Figure 2. For TMATT, the S atom in its molecule is the active center. Based on Pearson’s hard and soft acids and bases (HSAB) (Pearson 1963), Ca(II) is a hard acid, Cu(II) is a borderline acid, Cu(I) is a soft acid, and thiocarbonyl S is a soft base. Therefore, it is very clear that TMATT prefers to combine with Cu(II)/Cu(I) (in situ reduction of Cu(II)) rather than Ca(II), resulting in the selective flotation of TMATT to malachite against calcite.

### 4. Conclusions

The results of contact angle, micro-flotation, and bench-scale flotation indicated that TMATT exhibited stronger hydrophobization to malachite than OHA, and realized better flotation enrichment and separation of malachite against calcite and quartz.

---

**Table 3.** The concentration of elements on malachite surfaces.

| Elements             | Atomic ratio/% |
|----------------------|----------------|
|                      |
| C 1s                 | N 1s           | O 1s | S 2p | Cu 2p |
| Malachite            | 26.32          | 0.40 | 49.78| –     | 23.50 |
| Malachite adsorbed TMATT | 43.38         | 12.01| 29.62| 3.09 | 11.90 |
| Δ                  | 17.06          | 11.61| –20.16 | 3.09 | –11.60 |

$Δ$ is assigned as the difference between malachite and malachite adsorbed TMATT.

---

**Figure 8.** XPS high-resolution spectra of TMATT (a), TMATT-Cu$^{2+}$ sediments (b), and malachite without (c) or with (d) TMATT cover.
XPS, FTIR, AFM and zeta potential deduced that the adsorption of malachite toward TMATT rendered the reduction of its surface Cu(II) to Cu(I), and then the exocyclic N and S atoms of TMATT bonded with the Cu(I) to generate the TMATT-Cu(I) surface complexes on malachite. The superior hydrophobicity of TMATT and its favorable five-membered ring bonding mode on malachite might deserve its superior flotation response to malachite in comparison with OHA. Moreover, TMATT preferred to combine with surface Cu(II)/Cu(I) on malachite rather than Ca(II) on calcite, resulting in its selective flotation of malachite against calcite.

**Article highlights**

- TMATT was first used as a flotation collector to separate Cu oxide minerals.
- TMATT held better flotation selectivity to malachite against calcite than OHA.
- The exocyclic N and S atoms of TMATT bonded to the surface Cu(I) of malachite.
- TMATT preferred to bond with soft acid Cu(I) rather than hard acid Ca(II).
- TMATT-Cu(I) complexes own stronger hydrophobicity than OHA-Cu(II) complexes.

**Disclosure statement**

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the article.

**Funding**

The authors would like to thank the National Natural Science Foundation of China [51474253], the National Basic Research Program of China (973 program) [2014CB643403], and the National High Technology Research and Development Program of China (863 program)[2013AA064101] for the financial support.

**Supporting information**

The XRD (X-ray Diffraction) and XRF (X-ray fluorescence) for malachite, quartz and calcite, and the flowsheet of the locked-cycle flotation experiment were listed in the Supporting Information.

**References**

Abramov, A. A., and Forssberg, K. S. E., 2005, “Chemistry and optimal conditions for copper minerals flotation: theory and practice.” *Mineral Processing and Extractive Metallurgy Review*, 26(2). pp. 77–143. doi: 10.1080/08827500590883197.

Ahmed, N., and Jameson, G. J., 1989, “Flotation kinetics.” *Mineral Processing and Extractive Metallurgy Review*, 5(1–4). pp. 77–99. doi: 10.1080/08827508908952645.

Alim, G., 2007, “The role of Na2S2O5 and activated carbon on the selective flotation of chalcopyrite from a copper ore using a dithiophosphine-type collector.” *Mineral Processing and Extractive Metallurgy Review*, 28(3). pp. 235–245. doi: 10.1080/08827500601141750.

---

**Table 4.** The XPS bands parameters and characteristics of Cu 2p3/2, S 2p and N1s.

| Materials          | Elements | Binding energy/eV | FWHM/eV | Atomic ratio/% | Assignment       |
|--------------------|----------|-------------------|---------|----------------|-----------------|
|                    |          |                   |         |                |                 |
| TMATT              | S 2p     | 162.26/163.44b    | 1.17/1.17 | 66.67/33.33 | S_{TMATT}       |
|                    | N 1s     | 400.28            | 1.49    | 50.25          | C-NH-N=C        |
|                    |          | 401.36            | 1.61    | 49.75          | C-N{(NH}_{2}}C  |
| TMATT-Cu^{2+} sediments | Cu 2p3/2 | 932.24            | 1.66    | 100            | TMATT-Cu(I)     |
|                    | S 2p     | 162.54/165.72b    | 1.35/1.35 | 66.67/33.33 | S_{TMATT-Cu}   |
|                    | N 1s     | 399.26            | 1.38    | 50.25          | Cu-N=N=C        |
| Malachite          | Cu 2p3/2 | 934.68            | 2.71    | 100            | Cu(II)          |
| Malachite adsorbed | Cu 2p3/2 | 932.34            | 2.03    | 48.45          | TMATT-Cu(I)     |
| TMATT              | S 2p     | 934.79            | 2.64    | 51.55          | Cu(II)          |
|                    | N 1s     | 399.22            | 1.53    | 50.76          | C=N-N=C         |
|                    |          | 400.45            | 1.58    | 24.37          | Cu-N            |
|                    |          | 401.19            | 1.59    | 24.87          | C-N=C           |

* Full width of half maximum
b (S 2p3/2)/S 2p1/2
Ananthapadanabhan, K., and Somasundaran, P., 1985, “Surface precipitation of inorganics and surfactants and its role in adsorption and flotation.” Colloids and Surfaces, 13, pp. 151–167. doi: 10.1016/0166-6622(85)80014-7.

Bahrani, A., Ghorbani, Y., Hosseini, M. R., Kazemi, F., Abdollahi, M., and Danesh, A., 2018, “Combined Effect of Operating Parameters on Separation Efficiency and Kinetics of Copper Flotation.” Mining. Metallurgy and Exploration 1–13. doi: 10.1007/s42461-018-0005-y.

Bakalarz, A., Gloy, M., and Luszczkiewicz, A., 2015, “Flotation of sulfide components of copper ore in the presence of n-dodecane.” Mineral Processing and Extractive Metallurgy Review, 36(2). pp. 103–111. doi: 10.1080/08827508.2014.898381.

Barbaro, M., Urbina, R. H., Cozza, C., Fuerstenau, D., and Marabini, A., 1997, “Flotation of oxidized minerals of copper using a new synthetic chelating reagent as collector.” International Journal of Mineral Processing, 50(4), pp. 275–287. doi: 10.1016/S0301-7516(97)00045-8.

Bartos, P. J., 2002, “SX-EW copper and the technology cycle.” Resources Policy, 28(3–4). pp. 85–94. doi: 10.1016/S0301-7516(02)00025-4.

Booth, R. B., Hartjens, H., and Falavey, J. I., 1971, “Di (4–5 carbon branched primary alkyl) dithiophosphate promoters for the flotation of copper middlings.” U.S. Patent 3,707,457.

Buckley, A., Denman, J., and Hope, G., 2012, “The adsorption of n-octanoylhydroxamate collector on Cu and Fe oxide minerals investigated by static secondary ion mass spectrometry.” Minerals, 2(4). pp. 493–515. doi: 10.3390/min2040493.

Bulatovic, S., 2010, “Flotation of oxide copper and copper cobalt ores.” Handbook of Flotation Reagents: Chemistry, Theory and Practice, 2. pp. 47–65.

Celik, I. B., Can, N. M., and Sherazadishvili, J., 2010, “Influence of process mineralogy on improving metallurgical performance of a flotation plant.” Mineral Processing and Extractive Metallurgy Review, 32(1). pp. 30–46. doi: 10.1080/08827508.2010.509678.

Chebabe, D., Derraj, A., Erramli, H., and Haajaji, N., 2014, “Corrosion inhibition of bronze alloy B66 by 4-amino-3-methyl-1, 2, 4-triazole-5-thione in 3 per cent NaCl solution.” Anti-Corrosion Methods and Materials, 61(5). pp. 281–286. doi: 10.1002/ACMM.05-2013-1265.

Chen, X., and Peng, Y., 2018, “Managing clay minerals in froth flotation —A critical review.” Mineral Processing and Extractive Metallurgy Review, 39(5). pp. 289–307. doi: 10.1080/08827508.2018.1433175.

Cheng, X., and Iwasaki, I., 1992, “Pulp potential and its implications to sulfide flotation.” Mineral Processing and Extractive Metallurgy Review, 11(4). pp. 187–210. doi: 10.1080/08827509208914206.

Choi, J., Choi, S. Q., Park, K., Han, Y., and Kim, H., 2016, “Flotation behaviour of malachite in mono-and di-valent salt solutions using sodium oleate as a collector.” International Journal of Mineral Processing, 146. pp. 38–45. doi: 10.1016/j.minpro.2015.11.011.

Chufán, E. E., Pedregosa, J. C., and Borrás, J., 2013, “Branched primary alkyl) dithiophosphate promoters for the flotation of copper.” Metal Extractive, 7(3). pp. 3750–707.

Choi, J., Choi, S. Q., Park, K., Han, Y., and Kim, H., 2016, “Flotation behaviour of malachite in mono-and di-valent salt solutions using sodium oleate as a collector.” International Journal of Mineral Processing, 146. pp. 38–45. doi: 10.1016/j.minpro.2015.11.011.

Chufán, E. E., Pedregosa, J. C., and Borrás, J., 2013, “Branched primary alkyl) dithiophosphate promoters for the flotation of copper.” Metal Extractive, 7(3). pp. 3750–707.

Chufán, E. E., Pedregosa, J. C., and Borrás, J., 2013, “Branched primary alkyl) dithiophosphate promoters for the flotation of copper.” Metal Extractive, 7(3). pp. 3750–707.

Chufán, E. E., Pedregosa, J. C., and Borrás, J., 2013, “Branched primary alkyl) dithiophosphate promoters for the flotation of copper.” Metal Extractive, 7(3). pp. 3750–707.

Chufán, E. E., Pedregosa, J. C., and Borrás, J., 2013, “Branched primary alkyl) dithiophosphate promoters for the flotation of copper.” Metal Extractive, 7(3). pp. 3750–707.

Chufán, E. E., Pedregosa, J. C., and Borrás, J., 2013, “Branched primary alkyl) dithiophosphate promoters for the flotation of copper.” Metal Extractive, 7(3). pp. 3750–707.

Chufán, E. E., Pedregosa, J. C., and Borrás, J., 2013, “Branched primary alkyl) dithiophosphate promoters for the flotation of copper.” Metal Extractive, 7(3). pp. 3750–707.

Chufán, E. E., Pedregosa, J. C., and Borrás, J., 2013, “Branched primary alkyl) dithiophosphate promoters for the flotation of copper.” Metal Extractive, 7(3). pp. 3750–707.

Chufán, E. E., Pedregosa, J. C., and Borrás, J., 2013, “Branched primary alkyl) dithiophosphate promoters for the flotation of copper.” Metal Extractive, 7(3). pp. 3750–707.

Chufán, E. E., Pedregosa, J. C., and Borrás, J., 2013, “Branched primary alkyl) dithiophosphate promoters for the flotation of copper.” Metal Extractive, 7(3). pp. 3750–707.
Liu, G., Yang, X., and Zhong, H., 2016b, “New advances in the understanding and development of flotation collectors: A Chinese experience.” Minerals Engineering, 118. pp. 78–86. doi: 10.1016/j.mineng.2018.01.009.

Liu, G., Xiao, J., Liu, Q., Zeng, H., and Xu, Z., 2016b, “In situ probing the self-assembly of 3-hexyl-4-amino-1, 2, 4-triazole-5-thione on chalcopyrite surfaces.” Colloids and Surfaces A: Physicochemical and Engineering Aspects, 511. pp. 285–293. doi: 10.1016/j.colsurfa.2016.10.017.

Liu, G., Yang, X., and Zhong, H., 2017, “Molecular design of flotation collectors: A recent progress.” Advances in Colloid and Interface Science, 246. pp. 181–195. doi: 10.1016/j.cis.2017.05.008.

Liu, G., Zeng, H., Lu, Q., Zhong, H., Chai, P., and Xu, Z., 2012, “Adsorption of mercaptobenzothetacyclic compounds on sulfide mineral surfaces: A density functional theory study of structure-reactivity relations.” Colloids and Surfaces A: Physicochemical and Engineering Aspects, 409. pp. 1–9. doi: 10.1016/j.colsurfa.2012.04.036.

Liu, G., Zhang, H., Zhong, H., Liu, S., Zhao, G., and Xiao, J., 2015, “Preparation method of hydroxyamic acid or hydroxamic acid salt.” China patent CN 103929268B.

Liu, S., Zhong, H., Liu, G., and Xu, Z., 2018c, “Cu (I)/(Cu II) mixed-valence surface complexes of S-(2-hydroxyamino)-2-oxoethyln-N. Dibutylidithiocarbamate: hydrophobic mechanism to malachite flotation.” Journal of Colloid and Interface Science, 512. pp. 701–712. doi: 10.1016/j.jcis.2017.10.063.

Marion, C., Jordens, A., Li, R., Rudolph, M., and Waters, K. E., 2017, “An evaluation of hydroxamate collectors for malachite flotation.” Separation and Purification Technology, 183. pp. 258–269. doi: 10.1016/j.seppur.2017.02.056.

Nagaraj, D. R., and Farinato, R. S., 2016, “Evolution of flotation chemistry and chemistries: a century of innovations and the lingering challenges.” Minerals Engineering, 96. pp. 2–14. doi: 10.1016/j.mineng.2016.06.019.

Nath, M., Song, X., Eng, G., and Kumar, A., 2008, “Synthesis and spectral studies of organoiridium (IV) 4-amino-3-alkyl-1, 2, 4-triazole-5-thiones: in vitro antimicrobial activity.” Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 70(4). pp. 766–774. doi: 10.1016/j.saa.2007.09.009.

Park, K., Park, S., Choi, J., Kim, G., Tong, M., and Kim, H., 2016, “Influence of excess sulfide ions on the malachite-bubble interaction in the presence of thiol-collector.” Separation and Purification Technology, 168. pp. 1–7. doi: 10.1016/j.seppur.2016.04.053.