Study on recovery of iron and sulfur from high-sulfur magnetite ore

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Abstract: In this paper, to produce a saleable magnetite concentrate with a sulfur level below 0.20% and recover sulfur concentrate, flotation and magnetic separation tests were undertaken. Results showed that the optimum conditions of flotation were established as follows: grinding fineness of 90% particles passing 0.074mm, pH 6, 400 g/t of $CuSO_4$, and 400 g/t of combined collectors. Under these conditions and magnetic separation, S grade of the magnetite concentrate was reduced from 3.20% to 0.18%, and the Fe grade improved from 57.29% to 71.17%. At the same time a sulfur concentrate with S grade of 38.05% and recovery of 91.32% was also obtained. The XPS results showed that the addition of $CuSO_4$ benefited the formation of hydrophobic Sn2-/S0 and Cu+-xanthate, enhancing pyrrhotite floatability. The flotation separation efficiency could be enhanced using a mixture of collectors, and collector mixture demonstrated three synergetic effects, namely enhanced S recovery, improved adsorption behavior of the collectors and enhanced hydrophobicity of pyrrhotite surface.

Keywords: high-sulfur magnetite, pyrrhotite flotation, magnetic separation, mixed collectors

1. Introduction

Along with the rapid depletion of easy-to-process iron ores, exploitation of refractory ore has become increasingly important (Zhao et al., 2018). There is still a lot of high-sulfur magnetite around the world that has not been effectively developed because it tends to associate with some sulfide minerals, such as pyrite (FeS_2), pyrrhotite ($Fe_{1-x}S$) (Arvidson et al., 2013; Khoso et al., 2019; Yu et al., 2016).

Previous research showed that pyrite has some natural floatability and a small amount may be floated without collector (Han et al., 2018; Corin et al., 2018). In the presence of xanthate, 70 to 80% recovery of pyrite can be achieved by flotation in acidic to neutral pH conditions due to the formation of dixanthogen, while at other pH values, the recovery is much lower (He et al., 2011; Kelebek et al., 2007; Owusu et al., 2013). However, pyrrhotite can be rapidly oxidized when it is exposed to water or air giving unsatisfactory results (Chen et al., 2013; Allison et al., 2011; Bunkholt et al., 2015). In order to improve the recovery of pyrrhotite, some effective activators often need to add (Miller et al., 2005; Sajjad et al., 2015; Mu et al., 2016).

The formula of pyrrhotite is $Fe_{1-x}S$, where x varies from 0 to 0.125, and the ferromagnetic properties of pyrrhotite increases with S content increasing (Liu et al., 2018). The magnetism of pyrrhotite is similar to magnetite that can easily generate magnetic agglomeration leading to high content of sulfur in the iron concentrate (Becker et al., 2010). Therefore, it is a tough problem to separate pyrrhotite from magnetite by magnetic separation.

At present, flotation is considered to be the most effective method to remove pyrrhotite from magnetite. Early work on pyrrhotite flotation appeared to have concentrated on the use of a single collector. Silva et al. (2018) stated that xanthate is a good collector for pyrrhotite. Cui et al. (2021) also stated that flotation of pyrrhotite requires high collector dosage rates whether activator is used or not. However, previous studies have very few descriptions for the flotation recovery of sulfide minerals from high-sulfur magnetite. The available published data on separation of pyrrhotite from magnetite only indicates a decrease in sulfide minerals level to below 0.2%, but they did not give details on how

this was achieved (David et al., 2011and Kleiv C et al., 2021). Therefore, this paper describes the flotation work conducted to iron and sulfur from high-sulfur magnetite ore, and the influences of grinding fineness, pH, activator, collectors were studied. Finally, the mechanism of the flotation separation was also investigated..

2. Experimental

2.1. Materials and regents

The high-sulfur magnetite used in the study was obtained from West Africa. The sample was crushed to -1mm and then prepared for the experiment by using standard techniques. The chemical compositions of the sample are presented in Table 1. The content of Fe was 57.29%, and the content of S was 3.20%. The X-ray diffraction (XRD) pattern (Fig. 1) of the sample showed that the main minerals were magnetite (60%), pyrite (2%), pyrrhotite (4%), amphibole (12%), and small amounts of quartz.

Chemicals used in the flotation experiments included: dilute sulfuric acid (H_2SO_4) as pH regulator; sodium ethyl xanthate (SEX) and sodium iso-butyl xanthate (SIBX) as collector candidates; copper sulfate ($CuSO_4$) as activator and terpenic oil as a frother. Sulfuric acid and copper sulfate were of analytical grade and the rest were of industrial grade.

Table 1. Chemical analysis of the magnetite

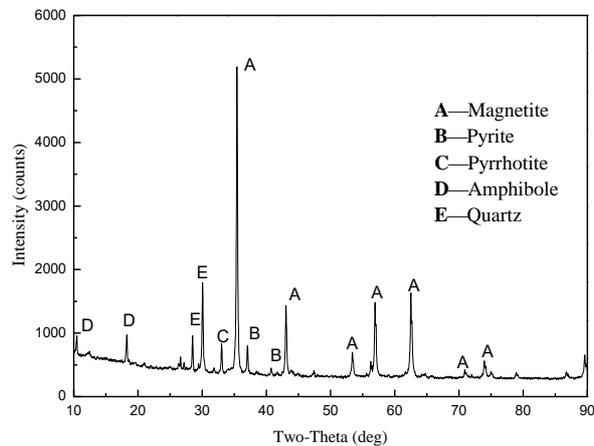| Composition	Fe	S	SiO_2	TiO_2	Al_2O_3	MgO	CaO	MnO	Na_2O	P_2O_5
Content wt.%	57.29	3.20	8.76	0.13	1.53	2.24	1.58	0.04	0.19	<0.1

Fig. 1. The XRD pattern of the magnetite

2.2. Froth flotation

Prepared samples of 150g were ground with a wet ball mill, and transferred directly to the 0.5 L XFG single-trough flotation cell. It was agitated at 1200 rpm for 5 min before any reagents were added. The flotation tests were conducted in accordance with the flowsheet shown in Fig. 2. First, the sample was added with a scheduled amount of pH regulator, and then activators were added into the pulp and conditioned for 3min. After this process, collectors were added, and the sample was conditioning for 3 min. Then, 60 g/t of terpenic oil was added before the froth was scraped. The rougher concentrate was collected for 6 min. In the scavenger flotation stage, the dosage of the reagents was the half of the rougher stage. Finally, the froth and tail samples were collected, filtered, dried, weighed and analyzed. The sulfur grade was analyzed by a carbon-sulfur analyzer (EMIA-110, Horiba). The flotation recovery was calculated based on the solid weight distributions between the flotation concentrate and the tailing.

2.3. Magnetic separation tests

When the bench-scale locked cycle tests finished, samples from flotation tailings were prepared, and then upgraded via a wet low intensity magnetic separator (XCGS-73). Finally, the magnetic product,

namely magnetite concentrate, was filtered and dried. Recoveries of S and Fe were calculated based on the solid weight distributions on the flotation concentrate, magnetic and non-magnetic products.
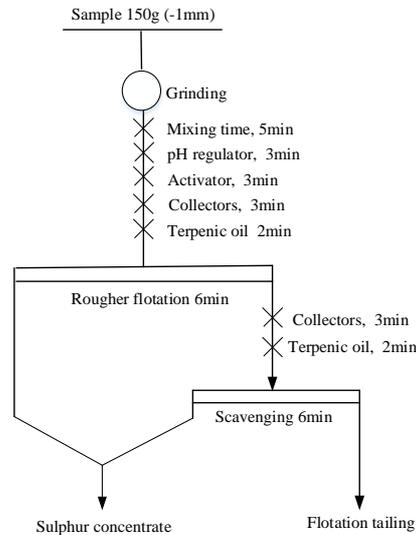

Fig. 2. The flowsheet of flotation separation tests

2.4. XPS and FTIR measurements

For each measurement, 2 g of mineral sample (< 20 μm) was placed in a 50mL beaker, and then 30 mL of 5 wt% hydrochloric acid was added to the beaker. The mineral surfaces were cleaned by using ultrasound cleaner for 30min to remove the oxidation film. After that, the mineral samples were filtered, washed with distilled water, and then the sample with corresponding flotation reagents was stored in a 50 ml beaker, and 30 ml of distilled water was added. The mixture was stirred for 20 min using a magnetic stirrer. Finally, the samples were filtered, dried, and analyzed.

The X-ray Photoelectron Spectroscopy (XPS) measurements were carried out using a Perkin-Elmer ESCA PHI 5400 spectrometer. The data processing was performed with XPS peak fitting software. The infrared spectrum was measured by the Fourier transform infrared spectrometer (NEZUS 470-FT-IR).

3.   Results and discussion

3.1. Effect of grinding fineness

Grinding fineness plays an important role in the flotation process. Thus, the effect of grinding fineness on the recovery of S was investigated. The results are presented in Fig. 3. Based on the dosage of reagents in previous research, the flotation conditions of rougher were set: pH 7.0, SEX 200 g/t and frother 60 g/t.

As shown in Fig. 3, the S grade in the concentrates increased as the grinding fineness was increased from 80% to 90%, but the value declined rapidly when the grinding fineness exceeded 90% mainly because excessive grinding produced too many fine particles, which reduced the efficiency of flotation. The S recovery was increased as the grinding fineness was increased. Therefore, the optimized grinding fineness was chosen as 90% particles passing 0.074 mm, the S grade was 21.81%, and their corresponding recovery was 45.41%. All subsequent flotation experiments were performed under this grinding fineness.

3.2. Effect of pH

Under the flotation condition of grinding fineness 90% -0.074 mm, SEX (200 g/t), and frother (60 g/t), the effects of pH values on the S recovery and grade in the concentrates were shown in Fig. 4. The S grade initially declined and subsequently increased when as the pH level increased, and the recovery values of S reached the maximum at pH 6.0. Thus, on the basis of the recovery, pH 6 was considered the best condition.
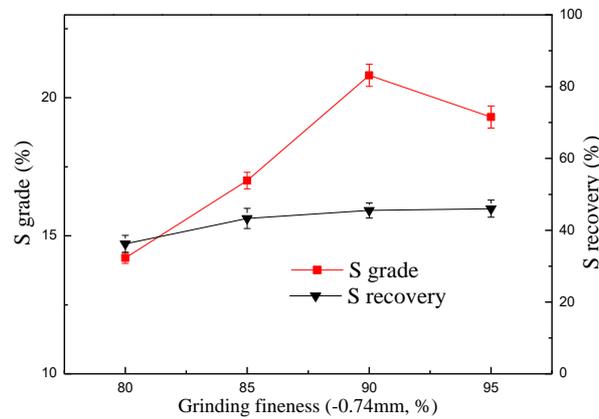
Fig. 3. The effects of grinding fineness on the S recovery and grade in the sulphur concentrates
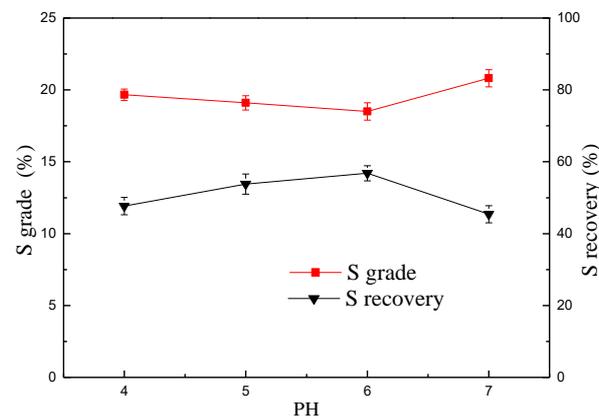

Fig. 4. Effect of different pH on the S recovery and grade in the sulphur concentrates

3.3. Effect of CuSO$_4$ dosage

The effects of CuSO$_4$ dosage on the recovery of S were investigated under the following conditions: grinding fineness 90% -0.074 mm, pH 6 and SEX 200 g/t. The results are presented in Fig. 5. As CuSO$_4$ dosage increased, the S grade and recovery initially increased and subsequently decreased. When the dosage of CuSO$_4$ was 400g/t, the recovery values of S reached the maximum, the S grade reached up to 19.43%, and the recovery was 82.53%. The results indicated that CuSO$_4$ were effective in the flotation, Fe2+ may be exchanged by Cu^{2+} on the surface of sulfide minerals (FeS$_2$, Fe1-xS), which helped improve the flotation (Ai et al., 2018; Tadie et al., 2017). However, adding more CuSO$_4$ did not improve flotation, probably because excessive copper(II) ions in the slurry caused the formation of an insoluble complex or killed the froth (Wiese et al., 2005; Bunkholt et al., 2015).
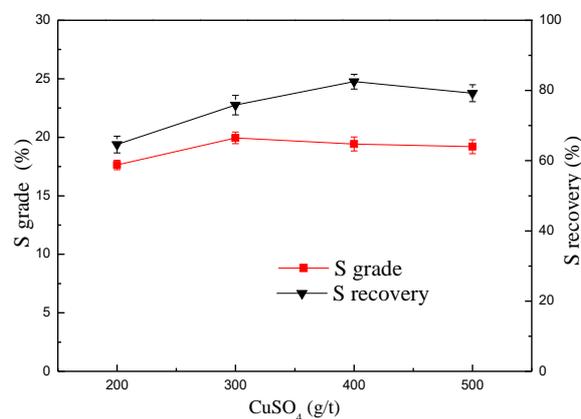

Fig. 5. Effect of CuSO$_4$ as activator on the S recovery and grade in the sulphur concentrates

3.4. Effect of collector dosage

The effects of different collectors (SEX, SIBX) on the recovery of S were investigated under the following conditions: grinding fineness 90% -0.074 mm, pH 6, and $CuSO_4$ 400 g/t. The results are presented in Fig. 6. The results indicated that all of the single collectors and mixed collectors were effective in S flotation, but they exhibit differences.
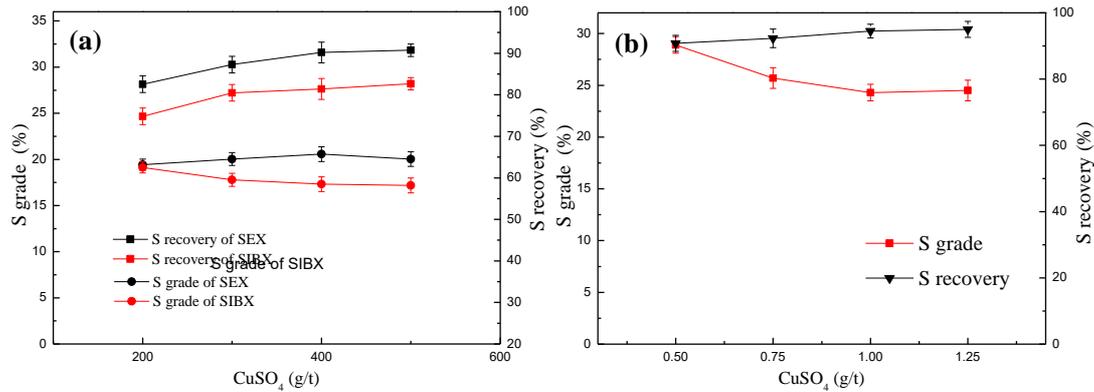

Fig. 6. Effect of different collectors on the S recovery and grade in the sulphur concentrates. (a) single collector (SEX and SIBX); (b) combined collectors of SEX and SIBX

Fig. 6 (a) shows that the effect of the single collectors on the S grade and recovery. It can be found that the S grade and recovery increased with the addition of SEX, but when the dosage of SEX was more than 400 g/t, they had little change. When the dosage of SEX was 400g/t, the S grade reached the maximum, the S grade reached up to 20.57%, and the recovery was 90.19%. In addition, with increasing SIBX dosage, the sulfur grade decreased, whereas the sulfur recovery increased. When the dosage of SIBX was 400g/t, the S grade was 17.18%, and the recovery was 82.66%.

The combined collector of SEX and SIBX was investigated when the dosage of collectors was 400 g/t, and the results are provided in Fig. 6 (b). The results indicated that the S recovery was higher than that of a single collector. As the proportion of SIBX increased, the S grade decreased and the recovery increased. When the mass ratio of SIBX to SEX was 1:1, the S grade was 24.23%, and its recovery was 94.28%, which indicated adding a mixture of SEX and SIBX can significantly increase sulfur recovery, and the mixture resulted in a recovery gain of 4–12% relative to the single collector. However, when the proportion of SIBX was further increased, the grade and the recovery had little change. Therefore, the best collector for recovering S was the combined collector of SEX and SIBX at an optimal mass ratio was 1:1, namely 200g/t SEX and 200g/t SIBX.

3.5. Open circuit flotation experiment results

Prepared sample was used for the open circuit flotation of sulfide minerals in this study. The detailed flowsheet and reagent scheme of the open circuit flotation are shown in Fig. 7. H2SO4 was used to adjust the pulp pH to 6, and the $CuSO_4$ dosage was 400 g/t. Using the 1:1 collector mixture of SEX and SIBX. The results showed that a sulfur concentrate assaying 39.95% S was produced at a S recovery of 59.03%, and the S grade of flotation tailing was decreased to 0.17%, which meet the target requirements of magnetite concentrate with sulfur level below 0.20%.

3.6. Locked cycle flotation test as well as magnetic separation

Based on the optimized flotation conditions and open circuit tests, the bench-scale locked cycle tests were performed. The results reported in Tables 2 are the averages of triplicate chemical analyses (measurement error=±5‰). The closed-circuit flotation system reached equilibrium after five cycles. The reported yields for the final concentrates and tailings are average values for the last three cycles (cycles five to seven), and the experimental errors for the yields are<4%. The products were filtered, dried, weighed, and analyzed.The results shows that the sulfur concentrate with the S grade of 38.05%, and recovery of 91.32% was obtained, and the Fe recovery of the sulfur concentrate was lower, only for
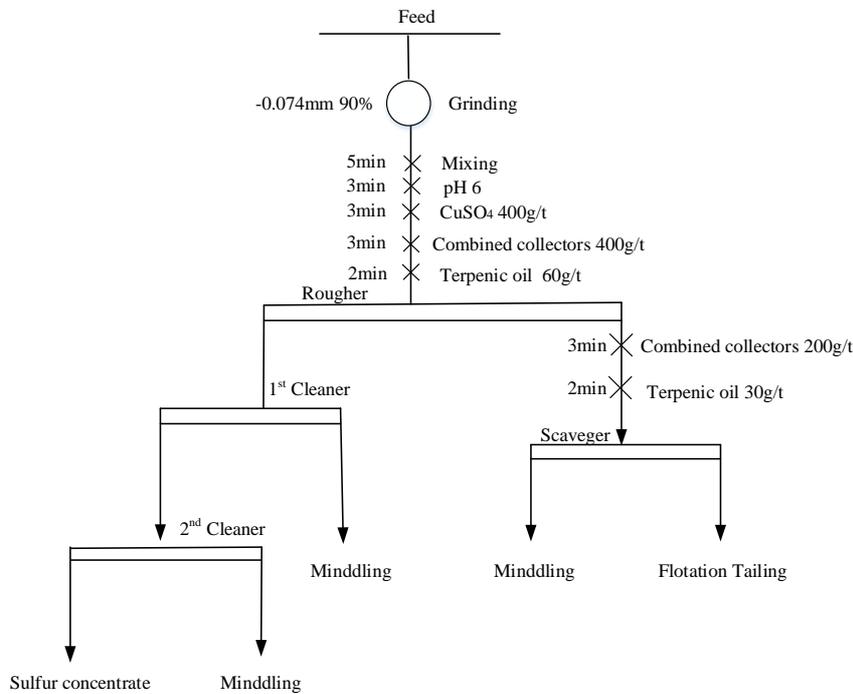
Fig. 7. The open circuit flowsheet of sulfur flotation (including the scheme of flotaion reagants)

6.52%. These results suggest that the developed flotation process effectively enriched the sulphide minerals from the magnetite ore. These flotation results also indicated that the combined collector of SEX and SIBX had the strongly collecting power for sulfide minerals and excellent selectivity against magnetite.

However, the S grade in the flotation tailing was still relatively high, and it remained higher than the product requirement. Magnetic separation may be required to reduce the sulphur below 0.2%. The flotation tailing was processed using wet low-intensity magnetic separation at magnetic intensity of 1200 Gs to decrease the grade of S. Table 2 shows the final product index after flotation–magnetic separation tests. The results showed that the sulfur grade of the magnetite concentrate decreased to 0.18% with the iron grade of 71.17% and the recovery of 83.84%.
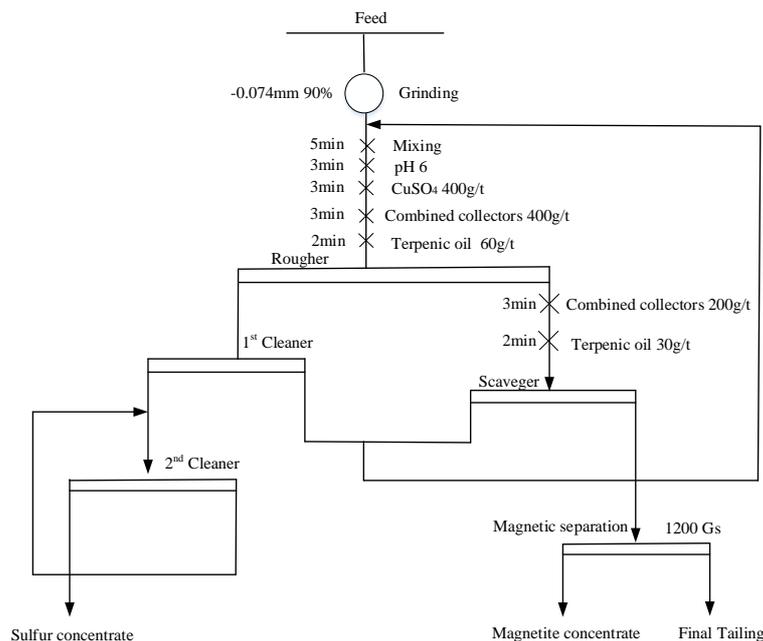
Fig. 8. Flowsheet and reagent scheme of the locked-cycle flotation and magnetic separation

Table 2. The results of the locked-cycle flotation tests

Products	Yield (%)	Grade (%)		Recovery (%)	
		S	Fe	S	Fe
Sulfur concentrate	7.68	38.05	48.66	91.32	6.52
Magnetite concentrate	67.49	0.18	71.17	3.80	83.84
Final tailing	24.83	0.63	22.23	4.88	9.64
Ore	100.00	3.20	57.29	100.00	100.00

4. Discussion

4.1. XPS analysis

 To find out the effects of activator and combined collector of SEX and SIBX on the flotation performance, the pyrrhotite was selected from the sample and the mechanism was investigated by XPS measurement. Fig. 9 shows the XPS spectra of the pyrrhotite with and without $CuSO_4$ and collectors treatment. Significant differences could be observed in terms of the elements (S, Cu and Fe) on the mineral surfaces. Pronounced changes were also observed in the atomic concentrations of the elements, as shown in Table 3.
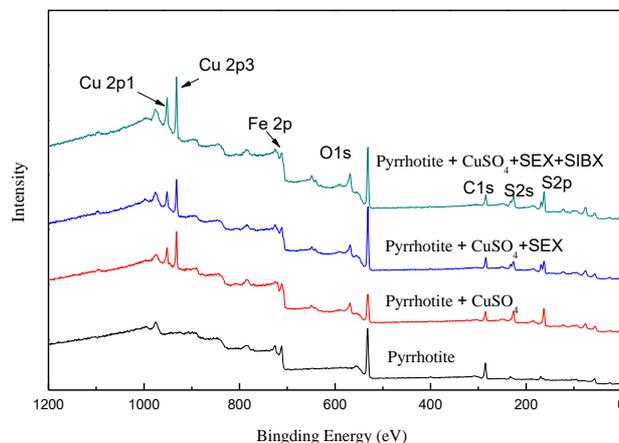

Fig. 9. XPS spectra from the surface of pyrrhotite untreated and treated with different reagents ($CuSO_4$, SEX and SIBX) at pH 6

Table 3 shows the surface atomic concentrations of the Fe, S, and Cu, before and after adding $CuSO_4$ and collectors. The addition of $CuSO_4$ increased the Cu concentration from 0% to 18.46% and the S concentration was also increased, but decreased the Fe concentration from 62.32% to 33.31%. This result suggests that Cu ions were adsorbed on the surface of pyrrhotite, probably because of the ion exchange reaction on the surface. With continuous addition of SEX and SEX+SIBX, the Fe concentration decreased, while the concentrations of Cu and S increased, which further indicated that collectors promoted the adsorption of Cu and S on the surface.

Fig. 10(a) shows that Cu 2p XPS spectra recorded from the surfaces of pyrrhotite before and after adding $CuSO_4$ and collectors. It can be found that when adding $CuSO_4$, a new component at the range of 930 to 935 eV was observed, and its peak area further increased when collectors (SEX/SIBX) were added.

The S2p XPS spectra from pyrrhotite surfaces after adding $CuSO_4$ are shown in Fig. 10(b). Fig. 10(b) indicated that the Cu^+ component was identified at about 932.2 eV, which was usually consistent with Cu^+–S compounds (Fairthorne et al., 1997). These results indicated that the present of $CuSO_4$ benefited the formation of stable complex Cu-xanthate which was one of the hydrophobic entities enabling pyrrhotite flotation.

Table 3. XPS derived surface concentrations (atomic % normalized to Fe, S, and Cu) on pyrrhotite surfaces in the presence of activator and collectors

Products	Yield (%)	Grade (%)		Recovery (%)	
		S	Fe	S	Fe
Sulfur concentrate	7.68	38.05	48.66	91.32	6.52
Magnetite concentrate	67.49	0.18	71.17	3.80	83.84
Final tailing	24.83	0.63	22.23	4.88	9.64
Ore	100.00	3.20	57.29	100.00	100.00
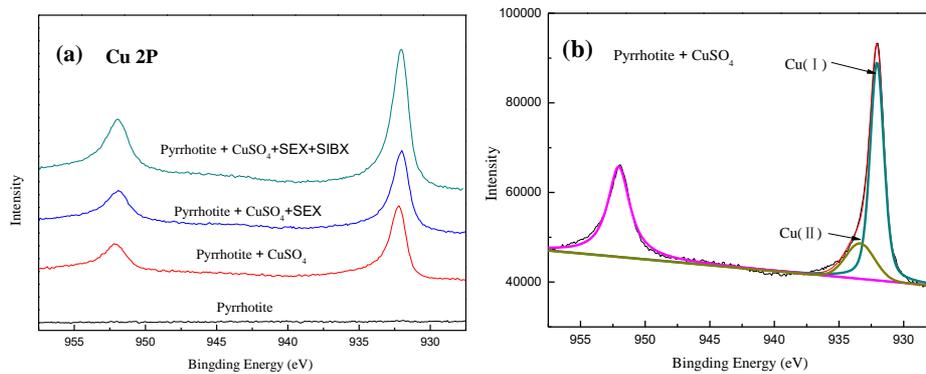
Fig. 10. Cu(2p) XPS from the surface of pyrrhotite. (a) the surface of pyrrhotite before and after adding $CuSO_4$ and collectors; (b) the surface of pyrrhotite after adding $CuSO_4$

The S 2p XPS spectra from pyrrhotite surfaces before and after adding $CuSO_4$ and collectors are shown in Fig. 11(a). A new component at the range of 161 to 164 eV was observed after the addition of $CuSO_4$, and another new component at the range of 168 to 170 eV was observed after the addition of collectors.

The S 2p XPS spectra from pyrrhotite surfaces after adding $CuSO_4$, SEX and SIBX are shown in Fig. 11(b). As shown in Fig. 11(b), the S(2p) bond energies of 161.6eV, 162.7eV, 164.8 eV were shown, which were usually consistent with sulfide(S_2^-), disulfide (S_2^{2-}), polysulfide and elemental sulfur (S_n^{2-}/S_0), while the other one at the higher binding energy range (168–169 eV) is due to formation of thiosulfate ($S_2O_3^{2-}$) and sulfate species(SO_4^{2-}) (Grano et al., 1997; Cao et al., 2018). These results suggest that in addition to ion exchange, there were also oxidation-reduction reactions; Cu(II) was adsorbed on pyrrhotite surfaces firstly, and then reduced to Cu(I) with the oxidation of S_2^{2-} to S_1^{1-} or S_n^{2-}. Therefore, when a mixed collector was added, adsorption behavior of the collectors was changed, and more Cu^+–xanthate, elemental sulfur and polysulfide were formed, enhancing pyrrhotite floatability.
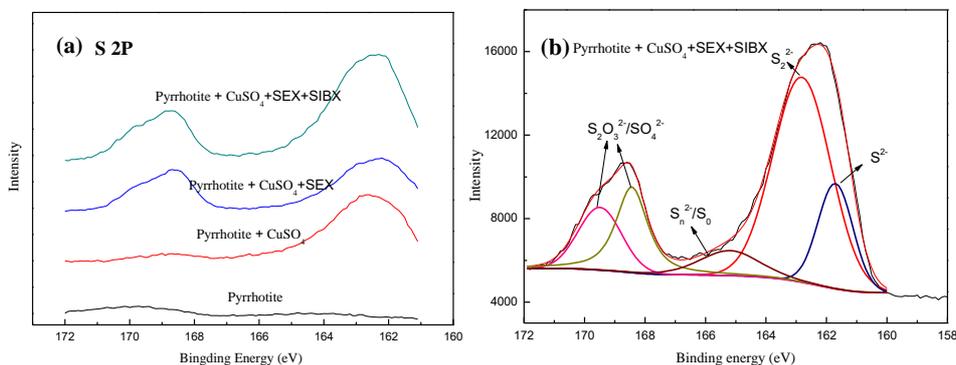

Fig. 11. S(2p) XPS from the surface of pyrrhotite. (a) the surface of pyrrhotite before and after adding CuSO4 and collectors; (b) the surface of pyrrhotite with CuSO4+SEX+SIBX

Fig. 12(a) shows Fe 2p XPS spectra recorded from the surfaces of pyrrhotite before and after adding $CuSO_4$ and collectors. It can be found that a new component at the range of 705 to 710eV was observed after adding $CuSO_4$ and collectors.

The Fe 2p XPS spectra from pyrrhotite surfaces after adding $CuSO_4$, SEX and SIBX are shown in Fig. 12(b). As shown in Fig. 12(b), a broad peak centered around 707.1eV, 710.5 eV can be assigned to Fe(II)-S, Fe(III)-O/OH species, respectively (Hao et al., 2019; Deng et al., 2018; Tian et al., 2018). It should be pointed out that FeOOH or Fe(OH)3 was generated through pyrrhotite oxidation, forming a hydrophilic film on the surface of pyrrhotite. This oxidation film would in turn prevent collectors from absorbing on the pyrrhotite surface, which can cause low sulfur recovery (Owusu et al., 2014).

However, a combined use of SEX and SIBX can significantly increase pyrrhotite flotation because the elemental sulfur, polysulfide and Cu-xanthate overweighed the hydrophilic Fe(III)-O/OH species on pyrrhotite surface. This can also explain why the flotation requires high dosage levels of collectors.
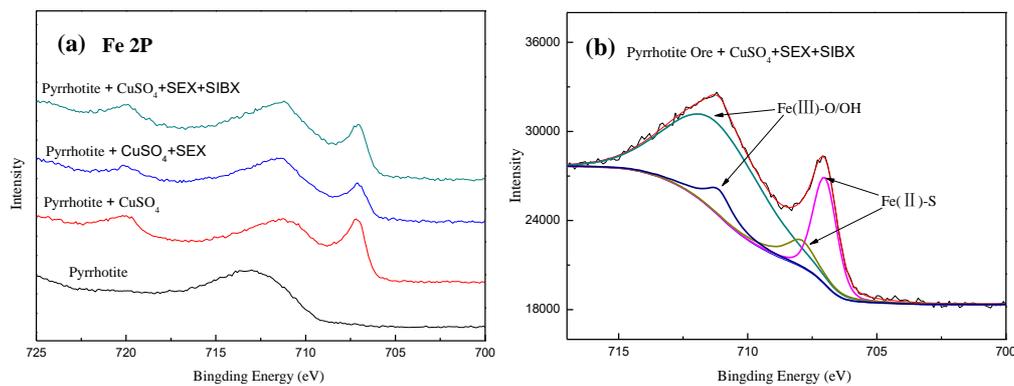

Fig. 12. Fe(2p) XPS from the surface of pyrrhotite. (a) the surface of pyrrhotite before and after adding $CuSO_4$ and collectors; (b) the surface of pyrrhotite with $CuSO_4$+SEX+SIBX

4.2. FT-IR analysis

The adsorption behavior of the flotation reagent on the pyrrhotite surface was explained by the change of the FTIR spectra of the pyrrhotite before and after the reaction with $CuSO_4$ and collectors. As shown in Fig. 13(a), after contacting with $CuSO_4$, no new band shifted and peaks were observed. After pyrrhotite was pretreated with $CuSO_4$ and SEX, the stretching band of -COC- at 1113 cm^{-1} shifted to 1120 cm^{-1}, and the stretching band of -C=S- at 1041 cm^{-1} shifted to 1034 cm^{-1}, indicating that the adsorption of SEX on pyrrhotite surface was a chemical adsorption. As shown in Fig. 13(b), after being treated with the mixed SEX/SIBX, the characteristic bands had no obvious changes and no new bands appeared compared with the spectrum of pyrrhotite treated by the single collector SEX, which suggests that the adsorption of SIBX on pyrrhotite surfaces may also have stronger physical adsorption in the mixed collectors SEX/SIBX solution.

Based on the FT-IR spectral analysis, it was concluded that compared with a single collector, the mixture of collectors enhanced chemical and physical adsorption, and a better balance of the distribution on pyrrhotite. Therefore, the flotation separation efficiency of S minerals could be enhanced using a mixture of collectors, and collector mixture demonstrated three synergetic effects, namely enhanced mineral recovery, improved adsorption behavior of the collectors and enhanced hydrophobicity of pyrrhotite surface.

5. Conclusions

1) The flotation results showed that the combined collectors of SEX and SIBX had the strongly collecting power for S minerals and excellent selectivity against magnetite. The optimum conditions were established as follows: grinding fineness of 90% particles passing 0.074mm, pH 6, 400 g/t of $CuSO_4$, the combined collector of SIBX/SEX at a dosage of 400 g/t.

2) Based on the locked cycle tests, S grade of the magnetite concentrate was reduced from 3.20% to 0.18%, and the Fe grade improved from 57.29% to 71.17%. At the same time a sulfur concentrate
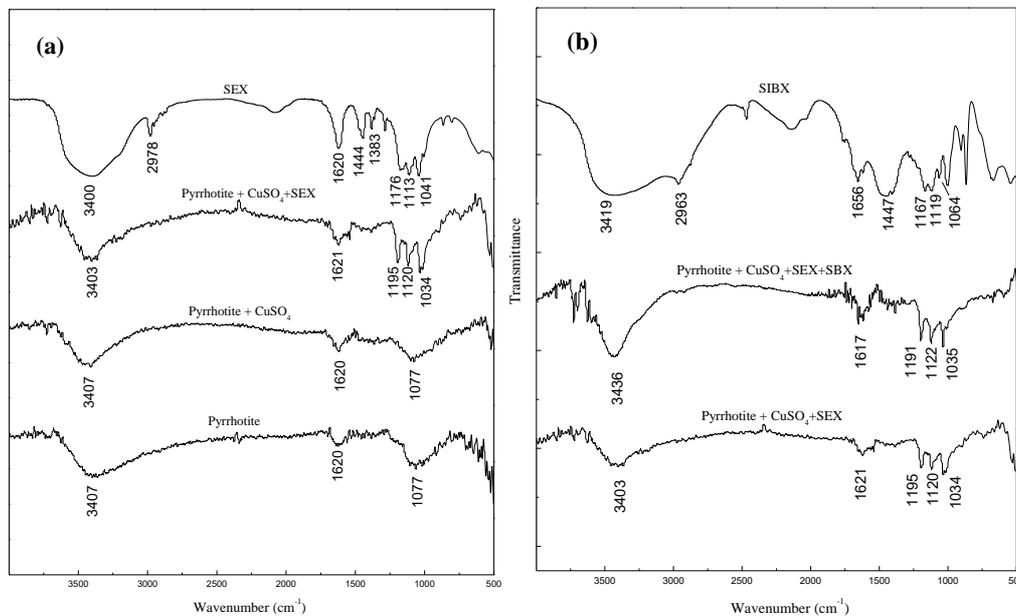
Fig. 13. The FTIR spectra of pyrrhotite untreated and treated with different reagents (CuSO$_4$, SEX and SIBX) at pH 6. (a) pyrrhotite untreated and treated with CuSO$_4$ and SEX; (b) pyrrhotite untreated and treated with single SEX, and mixed SEX/SIBX

with S grade of 38.05% and recovery of 91.32% was also obtained. The products met the target requirements.

3) The addition of CuSO$_4$ as activator facilitated the formation of hydrophobic S$_n^{2-}$/S0 and Cu$^+$-xanthate, enhancing pyrrhotite floatability. The flotation separation efficiency of S minerals could be enhanced using a mixture of collectors, and collector mixture demonstrated three synergetic effects, namely enhanced mineral recovery, improved adsorption behavior of the collectors and enhanced hydrophobicity of pyrrhotite surface.

Acknowledgement

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