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## Selective flotation separation of chalcopyrite and sphalerite by thermal pretreatment under air atmosphere

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**Abstract:** Thermal pretreatment was performed to enhance the flotation separation of chalcopyrite and sphalerite under the air atmosphere for the first time. Microflotation experiment showed that the floatability of chalcopyrite vanished after thermal pretreatment at above 170°C. By contrast, the floatability of sphalerite was well maintained with a flotation recovery of 90%. In artificial mixed mineral flotation experiments, the separation of sphalerite and chalcopyrite was successfully realized by thermal pretreatment. Results of Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy analyses indicated that the chalcopyrite surface was oxidized dramatically at 170°C, and hydrophilic species such as sulfate (SO<sub>4</sub><sup>2-</sup>), oxides (CuO and Fe<sub>2</sub>O<sub>3</sub>), and hydroxyl species (Fe(OH)<sub>3</sub>) were formed on the surface. Hence, the adsorption of potassium butyl xanthate on chalcopyrite decreased significantly after thermal pretreatment. The reason for the higher oxidation speed of chalcopyrite than that of sphalerite was also analyzed.

**Keywords:** thermal pretreatment, chalcopyrite, sphalerite, flotation, oxidation

### 1. Introduction

Chalcopyrite and sphalerite are the main copper- and zinc-bearing minerals, respectively (Liu et al., 2012; Bulatovic, 2007; Song et al. 2012). Copper is a highly valued non-ferrous metal that is widely applied in mechanical, electrical, metallurgical, and other industries (Chen et al., 2019; Ahmadi et al., 2010). Chalcopyrite (CuFeS<sub>2</sub>) is the major sulfide mineral for Cu extraction and contains about 70% of the total copper reserve globally among all types of copper-bearing ores in mineral processing (Mahajan et al., 2007; Chimonyo et al., 2020; Panda et al., 2015). Zinc is an important metal resource and is widely used in automobile, construction, ship-building, and light industries (Yahya et al., 2009; Kashani et al., 2008). Zinc is usually associated with other useful components, such as galena, copper sulfide, and other valuable minerals (Tan et al., 2010). Sphalerite and zinc oxide are the main zinc minerals. China has abundant copper and zinc resources. However, problems such as low ore grade and complex mineral composition have adverse effects on the efficient utilization of the resources.

Separation of copper and zinc has been a research hotspot and presents difficulty in mineral processing engineering. In grinding and flotation separation, copper ions can preactivate the surface of zinc sulfide and thus enhance the hydrophobicity; as such, "surface homogenization effect" occurs between copper sulfide and zinc sulfide. This phenomenon is one of the important reasons for difficulty in separation of copper and zinc sulfide (Lai et al., 2019; Dávila-Pulido et al., 2011; Khmeleva et al., 2005; Khmeleva et al., 2006).

Inorganic depressants are commonly used in traditional flotation for separation of copper and zinc. Cyanide is the most effective selective depressant of sphalerite in flotation. Nevertheless, the use of cyanide is restricted due to its severe environmental pollution and impact on the recovery of precious,

metals such as gold and silver (Chandraprabha et al., 2006). As a common depressant, zinc sulfate reduces the floatability of minerals by forming hydrophilic colloids on the surface of minerals, such as  $\text{HZnO}_2$  and  $\text{ZnO}_2^{2-}$  (Cao et al., 2006) in alkaline pulp. Another widely used class of depressant is sulfur-containing reagents, such as sulfites and bisulfates (Grano, et al. 1991), which are related to the formation of hydrophilic substances on mineral surfaces via chemisorption. Several researchers have proposed that sulfites can form hydrophilic surface layers of metals and consume copper ions in solution (Peres et al., 1979; Leia et al., 1982; Misra, et al. 1985). However, these common depressants are unsuitable for complex polymetallic sulfide ores in actual production (Yang et al., 2020). The use of such toxic or hazardous depressants is scrutinized due to increasingly stringent environmental pollution control regulations. In this regard, scholars have conducted numerous in-depth studies on organic depressants (Chen et al., 2013; Li et al., 2015; Anita et al., 2007; Liu et al., 2004; Drzymala et al., 2003; Ekmekci et al., 2004; Liu et al., 2000; Qin et al., 2013; Sarquis et al., 2014). Researchers have investigated the organic depressant sodium dimethyl dithiocarbonate (SDD,  $\text{C}_3\text{H}_6\text{NS}_2\text{Na}$ ), which has good selectivity for flotation of copper and zinc sulfide when used in combination with the conventional depressant zinc sulfate; however, the mechanism has not been elucidated yet (Qin et al., 2013). Locust bean gum can be adsorbed by hydroxyl with  $\text{ZnOH}$  or  $\text{ZnO}$  on the surface of oxidized sphalerite to reduce the floatability of sphalerite, thereby facilitating the separation of copper and zinc minerals (Feng et al., 2019). Yin (Yin et al., 2017) found that during Cu-Mo flotation separation, a PN: DT: DCMT mixture with a mass ratio of 1:1:1 could well replace NaCN as a chalcopyrite depressant to effectively reduce the floatability of chalcopyrite through chemical adsorption on the surface and has low toxicity and pollution. Current research and practice show that copper zinc sulfide ore organic depressant system has not been well elucidated and has few industrial applications reported. In addition, the flotation of copper and zinc sulfide ores often requires the combination of several depressants to achieve effective results (Yin et al., 2017). The activation of depressed minerals in subsequent flotation should also be considered.

Surface oxidation is also a sulfide mineral flotation depressing method; chalcopyrite surface oxidation methods include ozone oxidation,  $\text{H}_2\text{O}_2$  oxidation (Hirajima et al., 2017), plasma pretreatment (Hirajima et al., 2014; May et al., 2017), and Fenton-like oxidation (Wisnu et al., 2018; Suyantara et al., 2018). However, the oxidation degree of these methods is difficult to control, and the oxidant stability is poor. Moreover, residual collectors and foaming agents exist in the pulp or on the surface of the mineral; these organic reagents will increase oxidant consumption and lead to high oxidation cost. In this regard, a novel selective oxidation technology that uses a simple thermal pretreatment method for flotation separation of chalcopyrite and sphalerite was explored for the first time.

In the early stage, the author found that the floatability of copper sulfide minerals can be effectively depressed by thermal pretreatment. In the present work, the depression rule of thermal pretreatment on copper sulfide was evaluated through flotation experiments of single mineral and mixed minerals. The depression mechanism was further studied by combining Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) analyses.

## 2. Materials and methods

### 2.1. Samples and reagents

Natural chalcopyrite and sphalerite mineral samples were purchased from Zhejiang province, China. Mineral samples of  $-74 +38 \mu\text{m}$  fraction were prepared by crushing, dry grinding, and screening. According to X-ray diffraction and chemical analysis (Fig. 1), chalcopyrite and sphalerite samples have purity of 98.02% and 96.13%, respectively. Collector potassium butyl xanthate (PBX) were purchased from Shanghai Siyu Chemical Technology Co, Ltd. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used as pH modifiers. Analytical pure reagents and deionized water were used in all experiments, except for industrial-grade collector PBX.

### 2.2. Thermal pretreatment

Ore samples were subjected to laboratory-scale thermal pretreatment in a blast drying oven. For single-mineral flotation, 2 g of chalcopyrite and sphalerite samples were obtained and placed in different

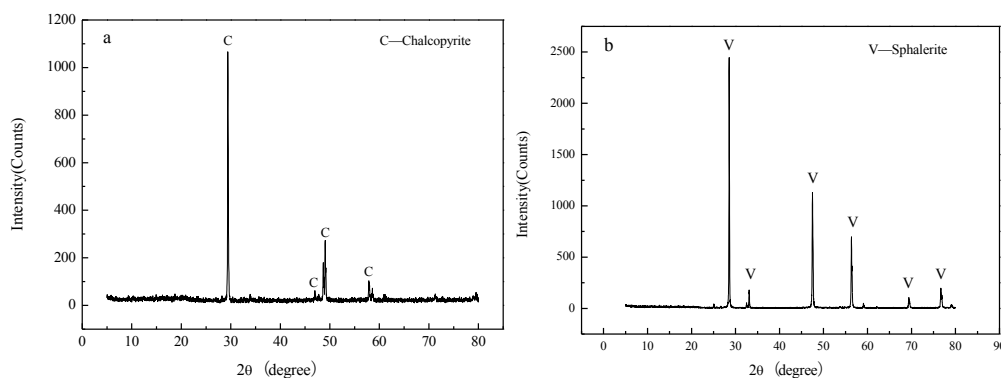


Fig. 1. XRD patterns of chalcopyrite and sphalerite pure minerals: (a) chalcopyrite and (b) sphalerite

porcelain boats. For mixed-mineral flotation, 1 g of chalcopyrite and sphalerite samples were obtained and placed in the same porcelain boat. The samples were calcined under pre-determined temperature in air atmosphere in a blast drying oven (DKM410C, Yamato scientific Chongqing CO., LTD.). When the predetermined temperature of the air in the oven was reached, the ore sample was immediately placed inside for 4 hours. The samples were then naturally cooled to room temperature and subjected immediately to flotation test.

### 2.3. Flotation tests

Microflotation experiments were conducted in XFG<sub>II5</sub> flotation machine (40 mL, Jilin Exploration Machinery Factory) with a Plexiglass cell at room temperature (Ca. 25°C). For each test, 2 g of single-mineral samples (or 1 g of chalcopyrite and sphalerite samples in artificial mixed-mineral flotation experiments) and 35 ml of deionized water were placed in the flotation cell and stirred for 1 minute. The solution of hydrochloric acid or sodium hydroxide was used to adjust the pH of the pulp, and the mixture was stirred for 5 minutes. The collector potassium butyl xanthate (PBX) was subsequently added and stirred for 3 minutes. Prior to flotation, the frother methyl isobutyl carbinol (MIBC) was added and stirred for 1 minute. Airflow was introduced to the cell by self-suction under 1900 rpm, and flotation was conducted for 3 minutes. For single-mineral flotation, recovery was calculated according to the dry weight of the flotation concentrate and tailings. For artificial mixed-mineral flotation experiments, Zn recovery was calculated according to the grade of concentrates and tailings.

### 2.4. FTIR analysis

The mineral samples and reagents were analyzed by AVATAR360 infrared spectrometer. After thermal treatment at 170 °C, 2 g of pure minerals and appropriate amount of deionized water were added into two beakers separately and stirred with a magnetic stirrer. The pulp pH of the first beaker was adjusted to 9.0, while the other beaker was retained at natural pH under stirring for 3 minutes. The collector was added to both beakers, and the mixture was stirred for 30 min. The samples were then separated by centrifugation. The sediment was rinsed with deionized water and dried in a vacuum drying oven. The background peaks of KBr were removed prior to the infrared study, and 1.0 mg of the sample was uniformly mixed with 100 mg of KBr particles. FTIR spectra were recorded within 4400–400 cm<sup>-1</sup> wavenumber.

### 2.5. XPS analysis

For XPS analysis, chalcopyrite samples in three porcelain boats were thermally treated at 170 °C. After thermal pretreatment, two of the samples were placed into the flotation cell. The pH of the pulp in the first flotation cell was adjusted, the collectors were added, and the mixture was stirred for 5 minutes. The samples were rinsed with deionized water three times, filtered, and dried in a vacuum oven for testing. The experiments were conducted using ESCALAB 250Xi (Thermo Fisher, USA) with monochromatic Al K $\alpha$  X-ray source. The energy step sizes for survey spectra and high-resolution XPS spectra were 1.00 and 0.05 eV, respectively. All elements were calibrated using C 1s.

### 3. Results and discussion

#### 3.1. Microflotation experiments results

##### 3.1.1. Effect of thermal pretreatment temperature on flotation recovery of chalcopyrite and sphalerite

The effect of thermal pretreatment temperature on the flotation of chalcopyrite and sphalerite at pH 9 was studied (Fig. 2). At pH 9, sphalerite exhibits good floatability and has recovery higher than 80% in a wide range of thermal pretreatment temperature. In comparison, the chalcopyrite recovery is only 3% after thermal pretreatment at 170 °C. The discrepancy could be due to the formation of the oxide film on the chalcopyrite surface after thermal pretreatment, which prevented the adsorption of the collector. Sphalerite was slightly affected in the entire thermal pretreatment temperature range. Therefore, the flotation separation of the two minerals may be realized through thermal pretreatment.

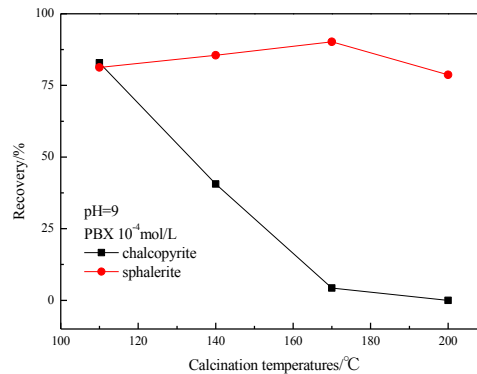


Fig. 2. Effect of thermal pretreatment on the flotation of chalcopyrite and sphalerite at different temperatures

##### 3.1.2. Effect of pH on flotation recovery of chalcopyrite and sphalerite

The effect of pH on the flotation of chalcopyrite and sphalerite after thermal pretreatment at 170°C was studied (Fig. 3). In the figure, pH has slight influence on the flotation recovery of sphalerite in a wide pH range. When pH reaches 0, the sphalerite recovery rate decreases to 77%. With increasing pH, the floatability of chalcopyrite sharply decreases, and the recovery decreases from 76.75% to 3%. Therefore, the depression effect of pH on chalcopyrite and sphalerite was disparate, which can significantly improve the separation effect of the two minerals.

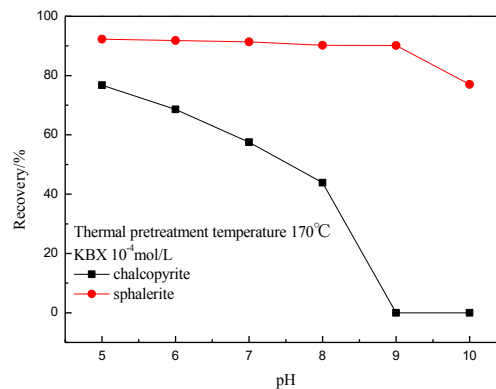


Fig. 3. Effect of thermal pretreatment on flotation of chalcopyrite and sphalerite at different pH levels

##### 3.1.3. Artificial mixed minerals flotation experiments

Two groups of artificial mixed-mineral flotation experiments were carried out. One of the groups of artificial mixed minerals was subjected to thermal pretreatment at 170 °C for 4 hours. In this experiment, the concentration of PBX was  $3 \times 10^{-5}$  mol/L, and the pH was 9.0.

As shown in Table 1, after thermal pretreatment, the Zn grade of concentrate reaches 83.44% and the recovery is 87.56%. When the samples were not thermally pretreated, the Zn grade of concentrate and

tailings is similar. Hence, chalcopyrite and sphalerite can be effectively separated in a binary mineral system by thermal pretreatment at 170°C for 4 hours.

Table 1. Flotation separation results of artificial mixed minerals

experimental condition	production	Yield (%)	Zn grade (%)	Zn recovery (%)
Thermal pretreatment	Concentrate	49.25	58.01	87.03
	Tailings	50.75	8.39	12.97
	Feed	100	32.83	100
untreated	Concentrate	75.40	32.83	76.33
	Tailings	24.60	31.21	23.67
	Feed	100.00	32.43	100.00

### 3.2. FTIR analysis

FTIR analysis was conducted to explain the effect of thermal pretreatment on the adsorption of collector on the mineral surface. The spectra of PBX are shown in Fig. 4a, and the spectra of chalcopyrite and sphalerite before and after treatment are shown in Fig. 4b-c, respectively.

The infrared spectrum of the collector PBX is shown in the Fig. 4. The peaks near 2957.76 cm<sup>-1</sup> are the asymmetric elongation vibration of -CH<sub>3</sub> and -CH<sub>2</sub> (Wang et al., 2015; Zhou et al., 2020). The peaks at 1159.62 and 1100.53 cm<sup>-1</sup> are the asymmetric stretching vibration and symmetric stretching vibration of C-O-C, respectively (Zhang et al., 2013). The absorption peak at 1467.70 cm<sup>-1</sup> is attributed to the stretching vibration of -C(=S)-S- (Huang et al., 2019). The absorption peak at 1069.32 and 664.44 cm<sup>-1</sup> are attributed to the stretching vibration of C=S and C-S, respectively (Wang et al., 1996; Zhang et al., 1997). For chalcopyrite (Fig. 4b), the adsorption peaks of PBX are observed at 1107.83 cm<sup>-1</sup> (xanthate copper) and 2976.51 cm<sup>-1</sup> (-CH<sub>2</sub>) (Khosro et al., 2019). The shift of these absorption peaks compared with PBX indicates that PBX is chemisorbed on the chalcopyrite surface. The FTIR spectrum showed that the stre-

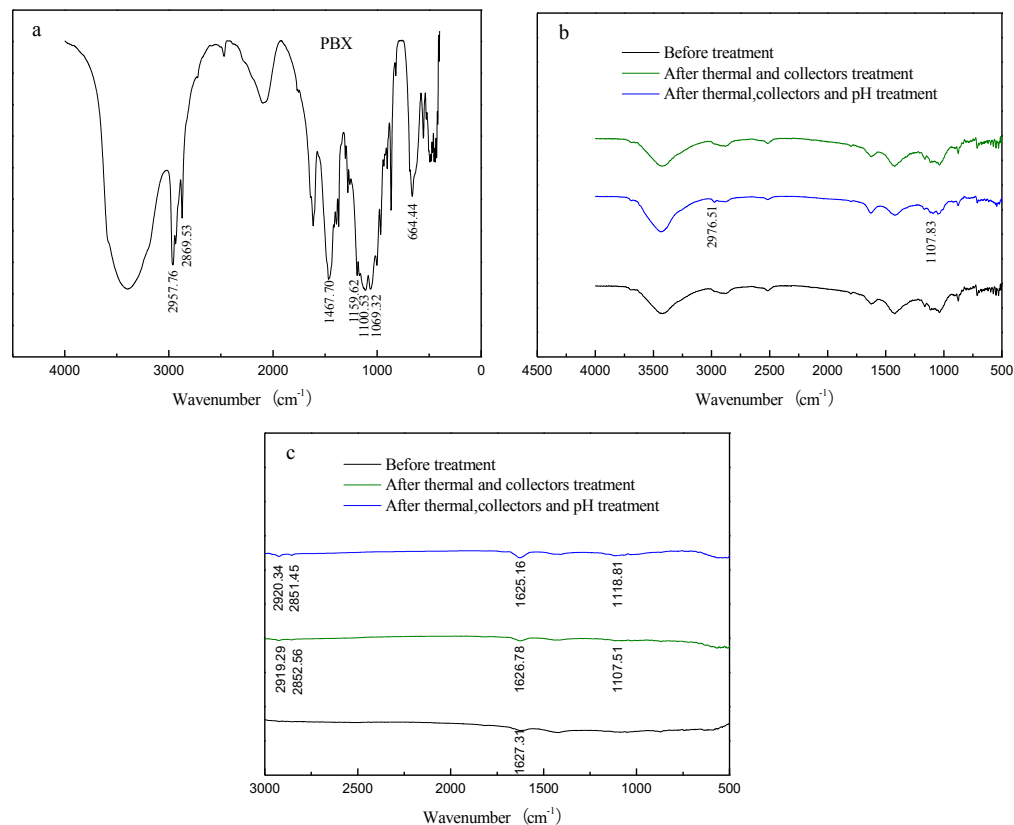


Fig. 4. FTIR spectra of PBX and two minerals under different conditions: (a) PBX, (b) chalcopyrite, and (c) sphalerite

ting vibration peak of PBX on the chalcopyrite surface disappears after thermal and NaOH treatment, indicating that the surface of chalcopyrite may be oxidized after thermal pretreatment. Hence, the adsorption of PBX on the chalcopyrite surface is poor, and the floatability of chalcopyrite vanishes after thermal pretreatment.

For sphalerite (Fig. 4c), the absorption peak of  $-\text{CH}_2$  at 2920.34 and 2019.29  $\text{cm}^{-1}$  appears on the sphalerite surface, and the absorption peak of the symmetric stretching vibration of  $-\text{CH}_2$  is observed at 2851.45 and 2852.56  $\text{cm}^{-1}$ . The stretching vibration absorption peak of C-S is also observed at 1118.81 and 1107.51  $\text{cm}^{-1}$ . The shifts of these absorption peaks indicate the chemisorption of PBX on the surface of chalcopyrite and sphalerite. The FTIR spectra show that the adsorption of PBX on the sphalerite surface is barely affected after thermal and NaOH treatment. Therefore, the floatability of sphalerite after thermal treatment did not change significantly.

The FTIR spectra show that the thermal pretreatment has a different effect on the adsorption of PBX on the chalcopyrite and sphalerite surface, thereby improving the separation effect of these minerals.

### 3.3. XPS analysis

XPS analysis was used to examine the chemical states of elements on the surface of chalcopyrite. Fig. 5 shows the XPS spectra of the minerals untreated and calcined at 170 °C for 4 hours, and the element contents in the mineral surface are shown in Table 2.

Table 2. Mineral contents in different situations

Elements	Content			
	Cu 2p	S 2p	C 1s	O 1s
Chalcopyrite	4.89	9.53	63.81	21.77
Chalcopyrite+170°C	1.24	2.96	74.98	20.82
Sphalerite	Zn 2p	S 2p	C 1s	O 1s
	15.32	14.15	56.52	14.01
Sphalerite+170°C	10.85	11.02	63.82	14.31

As shown in Table 2, after thermal pretreatment, the concentration of Cu 2p atom on chalcopyrite surface decreases from 4.89% to 1.24%, and the concentration of S 2p atom significantly decreases from 9.53% to 2.96%. In comparison, the concentration of Zn 2p atom on the sphalerite surface decreases from 15.32% to 10.85%, and the concentration of S 2p atom barely decreases from 14.15% to 11.02%. Hence, chalcopyrite and sphalerite were oxidized after thermal pretreatment at 170 °C. Obviously, the oxidation degree of the chalcopyrite surface is more serious than that of sphalerite.

Fig. 5 shows the high-resolution spectrum of Cu 2p, Fe 2p, S 2p, and O1s of chalcopyrite. Before thermal pretreatment, the separate peaks at 931.60 and 951.44 eV are identified as Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> of CuFeS<sub>2</sub> (Velásquez et al., 1998; Da Silva et al., 2018). The peaks at 708.20 eV is attributed to the Fe 2p of CuFeS<sub>2</sub> (Wisnu et al., 2018; Suyantara et al., 2018; Velásquez et al., 1998). The peaks at 160.75 and 162.05 eV correspond to S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub> peak of CuFeS<sub>2</sub> (Siriwardane et al., 1990). However, the two peaks centered at 931.97 and 951.57 eV correspond to the Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> of CuO, indicating that the surface of chalcopyrite was oxidized slightly before thermal pretreatment (Hirajima et al., 2014). The peaks of Fe<sub>2</sub>O<sub>3</sub> and the S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub> peaks of SO<sub>4</sub><sup>2-</sup> were observed at 711.44, 162.10, and 163.37 eV, respectively (Ozun et al., 2019; Siriwardane et al., 1990). According to Fig. 5d, the peaks of MeO and sulfate species of O 1s are found at 533.12 and 531.48 eV, respectively, indicating that Cu, Fe, and S of chalcopyrite react with O in air to some extent. All of above findings reconfirmed that chalcopyrite can be easily oxidized in air.

As shown in Fig. 5, the surface chemical states of chalcopyrite significantly change after thermal pretreatment. When the chalcopyrite is calcined, the peak strength of CuO, Fe<sub>2</sub>O<sub>3</sub>, and SO<sub>4</sub><sup>2-</sup> increases significantly, and the peaks shift to relatively higher binding energy due to the higher electronegativity of oxygen than sulfur (Tang et al., 2020). Additionally, the new peaks of SO<sub>4</sub><sup>2-</sup> appear at 168.68 and 16.83 eV, which indicates that the chalcopyrite surface underwent dramatical oxidation after thermal treat-

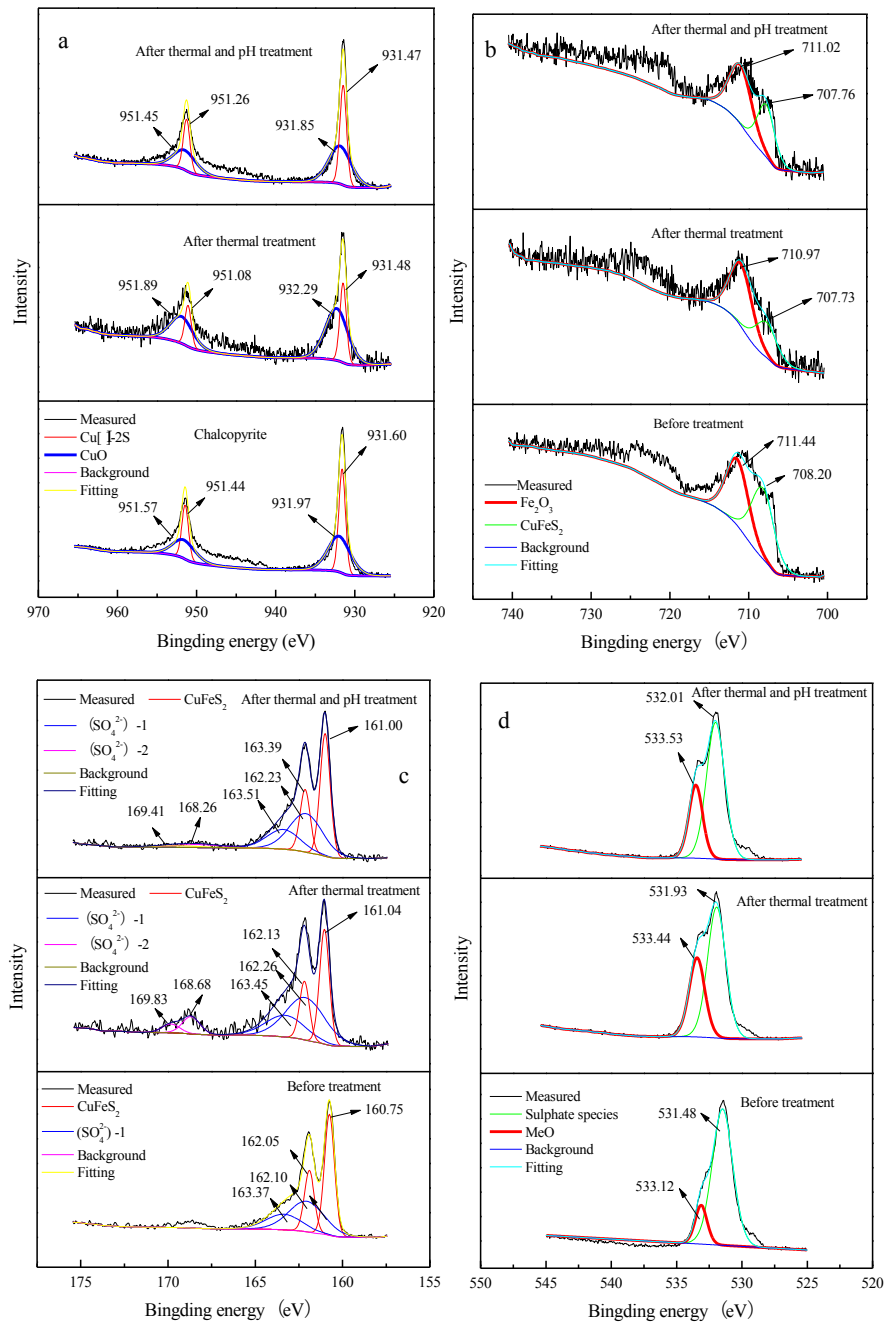


Fig. 5. High-resolution XPS spectra of the chalcopyrite before and after thermal pretreatment at 170 °C: (a) Cu 2p, (b) Fe 2p, (c) S 2p, and (d) O 1s

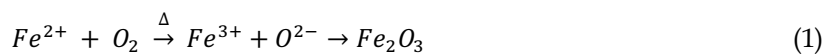
ment at 170°C. Furthermore, the strength of MeO peaks at 533.44 eV increases significantly, thereby confirming the occurrence of oxidation on the chalcopyrite surface.

When the pulp of chalcopyrite thermal-treated was adjusted by NaOH, the peak strengths of CuO and  $(\text{SO}_4^{2-})-2$  decrease due to the dissolution of CuO and sulfate. However, the peak strength of  $\text{Fe}_2\text{O}_3$  slightly changes, and the strength of the MeO peak at 533.53 eV is further enhanced, confirming that OH<sup>-</sup> in the solution reacts with Fe on the surface of chalcopyrite. Hence, the surface hydrophilicity of chalcopyrite was further enhanced, and the natural floatability vanished.

According to the FTIR and XPS analyses, surface oxidation by thermal pretreatment affects the flotation separation of minerals, but the reason why the surface oxidation degree of chalcopyrite is more serious than sphalerite remains unclear. We speculate that this phenomenon may be caused by the iron of chalcopyrite. The valence states of Cu and Fe of chalcopyrite and Zn of sphalerite are +2. However,

$\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  are in a relatively stable state. On the contrary,  $\text{Fe}^{2+}$  is unstable due to its certain reducibility. Hence,  $\text{Fe}^{2+}$  tends to take electrons from oxygen molecules and be converted to  $\text{Fe}^{3+}$ , which leads to the violent oxidation of chalcopyrite surface.

After thermal pretreatment and NaOH treatment, the following reactions possibly occur on the surface of chalcopyrite:



When chalcopyrite is calcined, the  $\text{Fe}^{2+}$  on the mineral surface is oxidized first and  $\text{O}^{2-}$  is produced. The S-Fe bonds and S-Cu bonds on the chalcopyrite surface are broken, and the chemical state of the elements on the mineral surface becomes out of balance. Hence,  $\text{O}^{2-}$  reacts with Fe, Cu, and S, and chalcopyrite is deeply oxidized. When NaOH solution is added in the pulp of chalcopyrite after treatment, the strong hydrophilic  $\text{Fe}(\text{OH})_3$  colloid is produced by the interaction of  $\text{Fe}^{3+}$  and  $\text{OH}^-$ , which prevents the adsorption of collector PBX on chalcopyrite and leads to the poor floatability of chalcopyrite.

#### 4. Conclusions

Effectively separating chalcopyrite and sphalerite without thermal pretreatment is difficult. Thermal pretreatment can selectively depress the flotation of chalcopyrite and effectively separate sphalerite. Thermal pretreatment had a strong depressive effect on chalcopyrite, but sphalerite maintained good floatability after thermal pretreatment in alkaline pulp. FTIR and XPS analyses showed that the surface of chalcopyrite had faster oxidation speed and higher oxidation degree than that of sphalerite under the same conditions. After thermal pretreatment, the adsorption of collector PBX on sphalerite in alkaline was barely affected, while the adsorption of collector PBX on chalcopyrite in alkaline was significantly affected due to the hydrophilic oxide film. Hence, the separation of chalcopyrite and sphalerite was realized in artificial mixed-mineral flotation experiments, and a concentrate with zinc grade of 58.01% and zinc recovery rate of 87.03% was obtained.

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