

# Improving the recovery of fine auriferous pyrite using iso-amylxanthate and its isomeride



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## ABSTRACT

The beneficial effects of the synergy between two reagents were realized long time ago. The purpose of using a mixture of collectors is to increase both the recovery and selectivity. In this work, sodium iso-amylxanthate (SIAX) and its isomeride (Y89), having different molecular structures, were used. The separation performance of these collectors were investigated at ratio varies of SIAX and Y89. The results showed that a better recovery of auriferous pyrite was observed with collector mixture comparing to use collector alone. There exist an optimal mass ratio between SIAX and Y89, and it is 1:2. The adsorption measurements of collector mixture and single collector were investigated at pH = 9, indicated that adsorption density of collector on auriferous pyrite surface was improved when collector mixture was used. Infrared spectral analysis suggested stretching vibration peaks from chemical adsorption were increased with using collector mixture. At an optimal mass ratio 1:2 of SIAX:Y89, an Au concentrate assaying 12.79 g/t was produced with an Au recovery of 84.24% from a feed containing only 3.44 g/t Au after one roughing stage. The advantage of this collector mixture can improve the recovery of auriferous pyrite at the same collector consumption, and this collector mixture has great potential for industrial application.

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## 1. Introduction

Gold is more commonly recovered together with sulfide minerals, and it is intimately associated with sulfides as fine unliberated grains (solid solutions or inclusions), or with barren and hydrophobic sulfides. The most commonly known gold bearing sulfides are the pyrite and arsenopyrite (Makanza et al., 2008).

All sulphhydryl collectors commonly are used in sulfide flotation, such as xanthates, dithiophosphates (DTPs) and dithiocarbamates (DTCs). These collectors are heteropolar and have aralkyl chain which is hydrophobic, as well as an ionized group containing sulfur, which reacts with water and is hydrophilic. The length and structure of this alkyl chain appears to have an effect on the behavior of the collector (Rao et al., 2003). Under certain redox conditions, both the xanthate and the dithiophosphate form their respective dimers, viz. dixanthogen and dithiophosphatogen, the latter less readily.

From the foregoing review of mechanisms, clearly any single collector will less than satisfactory in recovering auriferous pyrite because that fine particles have low collision efficiencies with gas

bubbles and float slowly (Bravo et al., 2005). The problem of recovering fine auriferous pyrite particles (<38 μm) continues to be a challenge for researchers working in this area (Valderrama et al., 1998; Forrest et al., 2001). Furthermore, mixtures of collectors are commonly used in flotation, and a range of performance benefits can be obtained (Lotter and Bradshaw, 2010; Chrysosoulis et al., 2004). This is a synergistic effect (Bradshaw, 1997). The synergistic enhancement of flotation performance observed has largely been attributed to improved adsorption characteristics of the collector mixture on the mineral surface as compared to those of the pure collectors. The improved adsorption characteristics would result in improved floatability by increasing the bubble-mineral attachment tenacity which would result in less mineral detachment and elutriation. The frother-collector interactions may also be increased resulting in stronger mineral-bubble attachment. Hangone et al., 2005, reported that the mixed collector system produced a more stable froth because of the increased hydrophobicity and wider range of particle sizes held in that froth.

For example, testwork reported by Glembotskii, 1958, showed that when a weaker collector is added to a stronger collector, the mixture results in a recovery gain of 2–5% relative to the single strong collector system. Glembotskii explained that the consistent better performance by the mixed collectors was due to the synergy effect generated between the two different collectors. He claimed

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that the larger the difference in structure and composition, the larger the synergy effect. Similarly, Alim et al., 2012, showed that mixtures of ethyl xanthate with diethyl dithiophosphate or ethyl dithiocarbamate resulted in large improvements in the flotation rate and recovery with pure galena in a microflotation cell. There have been numerous reports on flotation of auriferous pyrite using the mixture of the two different collector. However, a mixture collector of xanthate and its isomeride has not been extensively studied.

In this study, the flotation of fine auriferous pyrite particles (<38  $\mu\text{m}$ ) was studied with a collector mixture of Sodium iso-amylxanthate (SIAX) and its isomeride (Y89). The mechanisms underlying the mineral-reagent interaction were further investigated by adsorption measurements and infrared spectral analysis. The results provide a reference for effectively recovering fine auriferous pyrite before smelting.

## 2. Materials and methods

### 2.1. Pure minerals and reagents

Pure auriferous pyrite, sericite, quartz and dolomite were sourced from Xinjiang, China. X-ray powder diffraction data confirmed that the auriferous pyrite, sericite, quartz and dolomite were 97%, 95%, 98% and 96% pure, respectively. According to the results of chemical analysis, the content of Fe, S and Au was 42.37%, 45.33% and 290.64 g/t in pure auriferous pyrite, respectively. Molecular structure of auriferous pyrite is  $\text{FeS}_{1.863}$ . X-ray diffraction of auriferous pyrite, sericite, quartz and dolomite are shown in Fig. 1. The  $-38 \mu\text{m}$  fraction was used in the flotation tests.

The sources of flotation reagents were as follows: analytical grade sodium iso-amylxanthate (SIAX) and Y89 were from Zhuzhou flotation reagents factory, Hunan, China. The molecular of col-

lectors are shown in Fig. 2. The pH was adjusted with NaOH or HCl stock solutions. Deionized water with a resistivity of more than  $18 \text{ M}\Omega \times \text{cm}$  was used for all experiments.

### 2.2. Flotation experiment

Single mineral flotation tests were carried out in an XFG flotation machine with a 40 mL plexiglass cell, at an impeller speed of 1800 rpm. The mineral suspension was prepared by adding 3.0 g of minerals to 40 mL of distilled water. The pH of the mineral suspensions were first adjusted by adding NaOH or HCl. Once the desired reagent was added, the suspension was agitated for 3 min and the pH was measured before flotation. The flotation lasted for 4 min before the products were collected, dried, and weighed. The recovery was calculated based on the weights of the dry products obtained.

### 2.3. Adsorption measurements

The adsorption measurements were completed on a TU-1810 ultraviolet visible spectrophotometer (Purkinje General, Beijing, China). The curves represent the averages of five measurements, and the error bars are based on the standard deviation. Two grams of auriferous pyrite powder and 40 mL of distilled water were transferred into an Erlenmeyer flask. The particle size of auriferous pyrite powder was less than  $38 \mu\text{m}$ . After the reagent addition to the solution, the Erlenmeyer flask was stirred on a magnetic mixer for 1 h, allowing the adsorption process to reach equilibrium. The solution was centrifuged and filtered, and the supernatant was collected for UV spectrometry analysis. According to the residual concentration of the reagent remaining in the solution, the adsorption of the reagent on the mineral surface can be calculated as follows:

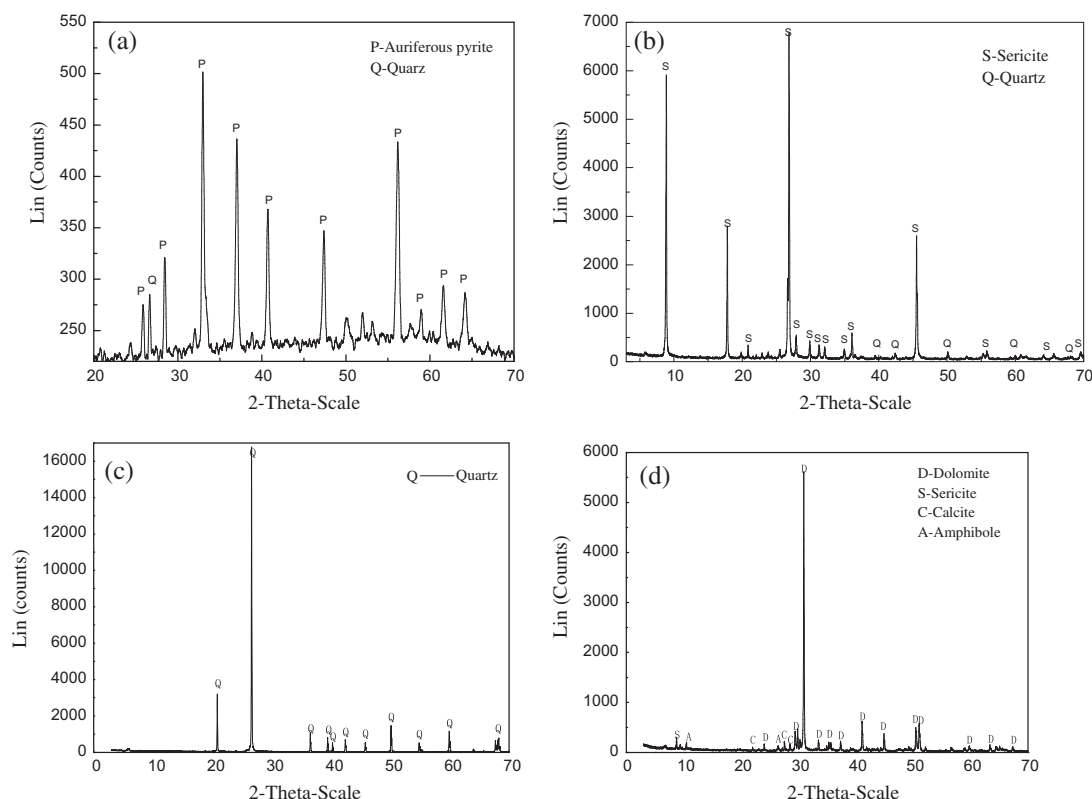


Fig. 1. X-ray diffraction of auriferous pyrite, sericite, quartz and dolomite.

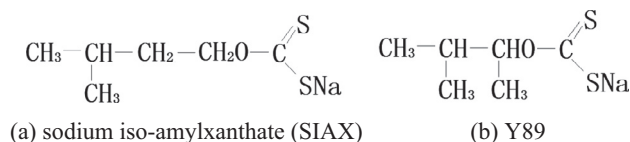


Fig. 2. Generic molecular structure of SIAX and Y89.

$$\Gamma = \frac{C_0 - C \times V}{m} \quad (1)$$

where  $\Gamma$  is the adsorption amount, mol/g;  $C_0$  is the initial concentration of reagent in the solution, mol/L;  $C$  is the residual concentration of the reagent in the supernatant, mol/L;  $V$  is the volume of the solution, L; and  $m$  is the weight of the mineral, g.

#### 2.4. Infrared spectral analysis

Prior to the test, pure minerals were ground to  $-2 \mu\text{m}$  in an agate mortar before they were conditioned with reagent in the solution. The fully interacted sample was filtered and washed three times with the corresponding pH solution. The solid obtained was dried in a vacuum desiccator. Fourier transform infrared spectra were recorded with a Nicolet™ 740 FTIR spectrometer (Thermo Scientific, Waltham, MA, USA) at  $25^\circ\text{C}$  in the range of  $4000\text{--}500 \text{ cm}^{-1}$ .

### 3. Results and discussions

#### 3.1. Microflotation

Firstly, the flotation separation tests using SIAX or Y89 at a dosage of 30 mg/L were evaluated by single mineral test, respectively. Flotation results show that, although high recovery of auriferous pyrite could be obtained at pH 4, the preferred pulp pH range using SIAX and Y89 as individual collector for auriferous pyrite flotation is 9–10 because that dolomite exists in this material. As shown in Fig. 3, pH = 9 was further used for all flotation tests.

As shown in Fig. 3(a), using SIAX alone as collector and Terpenic oil as frothing agent, a better result of auriferous pyrite flotation could be achieved when the SIAX concentration is higher than 40 mg/L. When SIAX concentration is 40 mg/L, the recovery of auriferous pyrite is 73.98%. Fig. 3(b) shows the similar flotation regularity when Y89 is used as collector, but Y89 shows much stronger collecting capacity than SIAX at the same consumption. When Y89 concentration is 40 mg/L, the recovery of auriferous pyrite is 75.25%.

From Fig. 4(a) and (b), it can be noted that auriferous pyrite has good floatability with Y89 and SIAX, indicating that Y89 is a better

collector for auriferous pyrite than SIAX. Also, 40 mg/L of collector concentration is enough for recovering auriferous pyrite.

The flotation behavior of auriferous pyrite, sericite, quartz and dolomite individually using a collector mixture of SIAX and Y89 at different mass ratio was investigated. A series of flotation results demonstrate that the collector mixture of SIAX and Y89 at a mass ratio of 1:2 achieves the best flotation separation performance, as shown in Fig. 5. Auriferous pyrite has a favorable recovery of 85.19%. Compared with the results using SIAX and Y89 as individual collector in Fig. 5, marked differences in the recovery of auriferous pyrite implies that the flotation separation performance is improved using 1:2 collector mixture SIAX + Y89.

As shown in Fig. 6, using SIAX + Y89 as mixed collector and Terpenic oil as frothing agent, a better result of auriferous pyrite flotation could be achieved when the concentration of mixed collector is higher than 40 mg/L. At the point of 40 mg/L of mixed collector, the recovery of auriferous pyrite is 85.19%. Further increasing concentration of mixed collector, recovery of auriferous remains almost unchanged, but recovery of dolomite will increase slightly.

From Fig. 5, it can be noted that the two strong collectors mixed is benefit for further increasing their collecting capacity at the same concentration. There exist an optimal mass ratio between two collector.

#### 3.2. Adsorption measurements

A series of adsorption studies were completed to probe the adsorption behavior of the single collector and mixed collector.

Fig. 7 illustrates that the adsorption density of SIAX on auriferous pyrite decreases from  $0.69$  to  $0.46 \text{ mg g}^{-1}$  as increasing the pH of pulp from 4 to 12. On the surface of auriferous pyrite, the adsorption amount of SIAX decreases slightly when the pH rises from 4 to 9. However, a sharp drop in the adsorption density of SIAX occurred at  $\text{pH} > 9$ . The adsorption density of Y89 on auriferous pyrite decreases from  $0.71$  to  $0.56 \text{ mg g}^{-1}$  as increasing the pH of pulp from 4 to 12. Although the adsorption density of Y89 has the same shape with SIAX, Y89 collector has much stronger adsorption capacity on the surface of auriferous pyrite in the whole pH range.

Adsorption studied were conducted on auriferous pyrite when the collector mixture of SIAX and Y89 was at a mass ratio of 1:2. As shown in Fig. 9, the adsorption density of mixed collector on auriferous pyrite decreases from  $0.80$  to  $0.63 \text{ mg g}^{-1}$  as increasing the pH of pulp from 4 to 12. Comparing to use collector alone, the mixed collector has better adsorption capacity on the surface of auriferous pyrite. That is the reason why the higher recovery of auriferous pyrite can be obtained when the mixed collector is used.

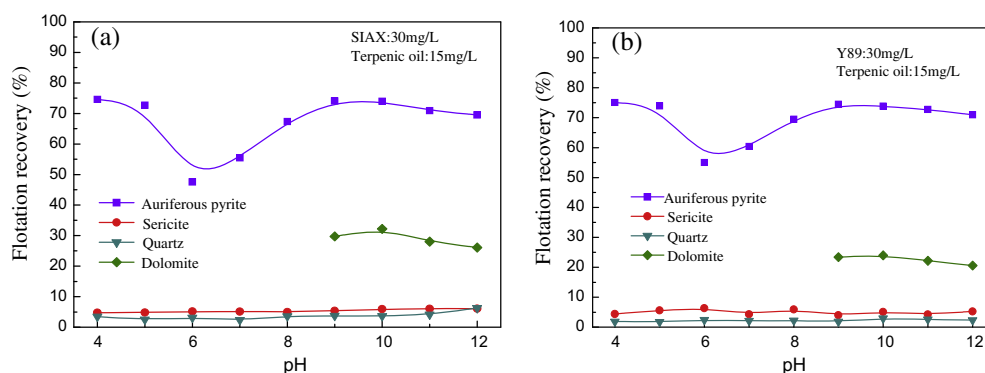


Fig. 3. Effect of pulp pH on flotation behavior of auriferous pyrite, sericite, quartz and dolomite using SIAX or Y89 as collector.

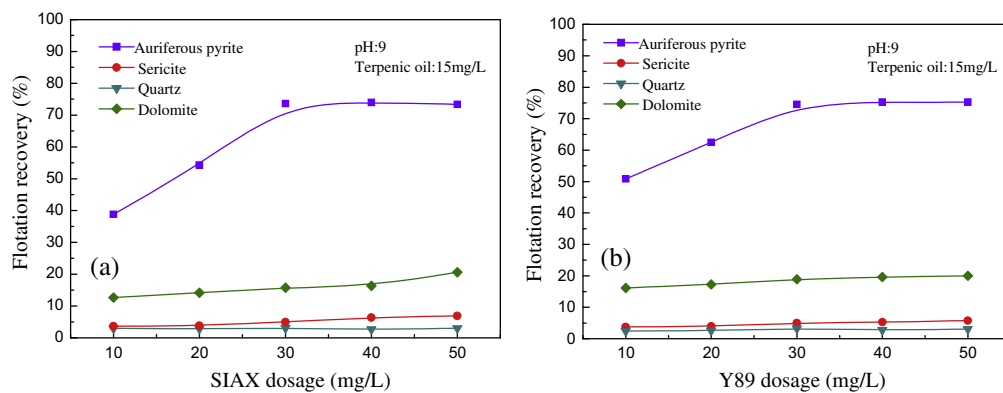


Fig. 4. Effect of SIAX dosage on flotation behavior of auriferous pyrite, sericite, quartz and dolomite.

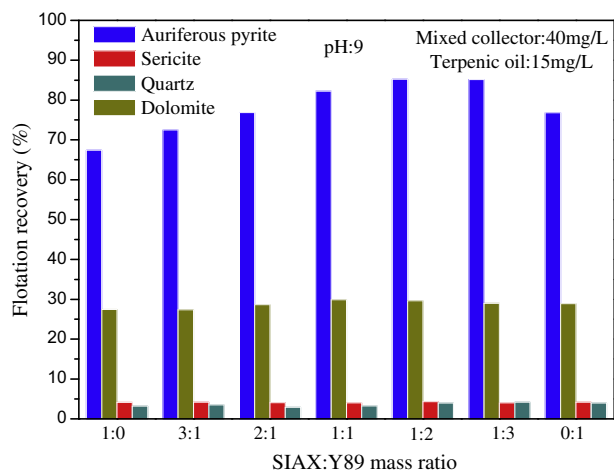


Fig. 5. Effect of mass ratio of SIAX + Y89 on flotation behavior of auriferous pyrite, sericite, quartz and dolomite.

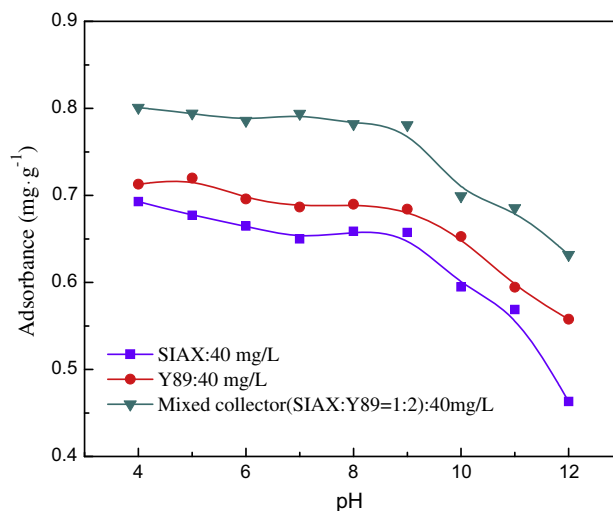


Fig. 7. Relationship between adsorbance of different collectors on auriferous pyrite and pulp pH.

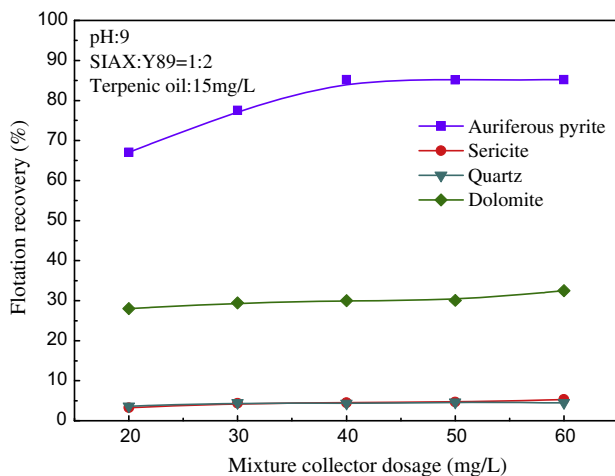


Fig. 6. Effect of mixed collector (SIAX:Y89 = 1:2) dosage on flotation behavior of four minerals.

### 3.3. Infrared spectral analysis

Fig. 8 shows the infrared spectral patterns of auriferous pyrite before and after interaction with SIAX. Fig. shows that, 2956.15 cm<sup>-1</sup> and 2874.08 cm<sup>-1</sup> are stretching vibration absorption peaks of C—H in —CH<sub>3</sub> and —CH<sub>2</sub>, respectively. 1146.01 cm<sup>-1</sup>

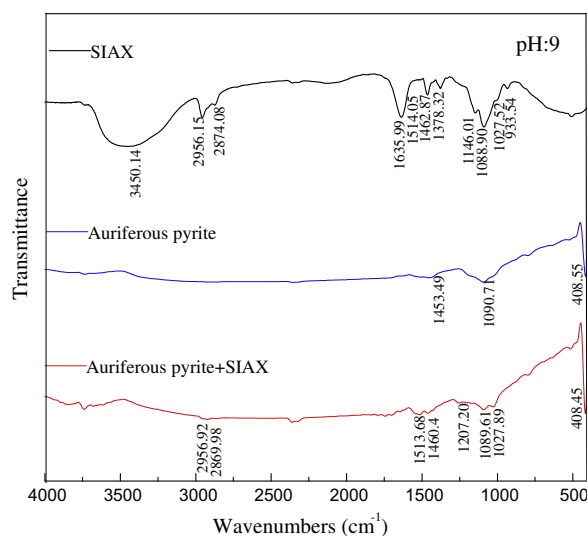


Fig. 8. IR spectrum in the absence and presence of pure SIAX.

is stretching vibration absorption peaks of C—O—C, 933.54–1027.52 cm<sup>-1</sup> are stretching vibration absorption peaks of C=S (Sun et al., 2014; Sun et al., 2015). IR spectrum of auriferous pyrite

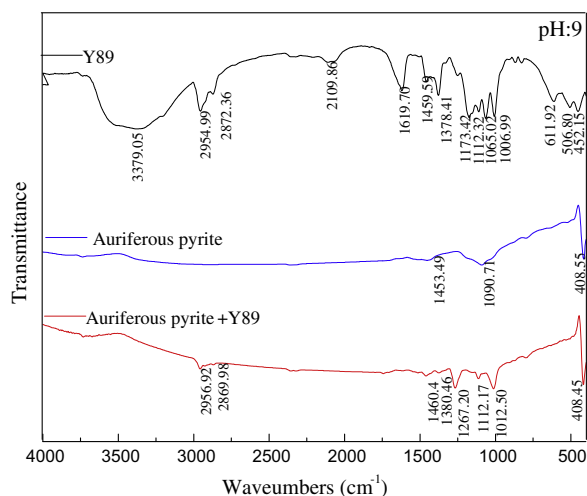


Fig. 9. IR spectrum in the absence and presence of pure Y89.

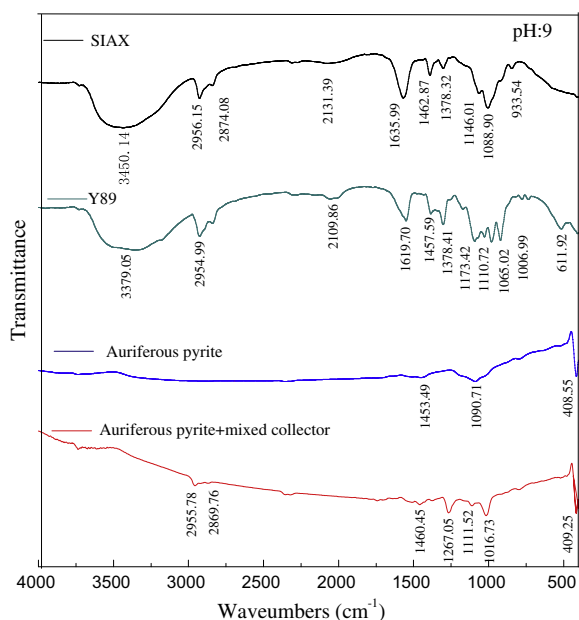


Fig. 10. IR spectrum in the absence and presence of mixed collector.

in Fig. 8 is consistent with the standard spectrum of pyrite, and there are three characteristic absorption peaks such as  $408.55\text{ cm}^{-1}$ ,  $1090.71\text{ cm}^{-1}$  and  $1453.49\text{ cm}^{-1}$ . Compared different spectrums in Fig. 8, stretching vibration peaks of C–H in  $2955.35\text{ cm}^{-1}$  and  $2852.72\text{ cm}^{-1}$  are found in the IR spectrum of auriferous pyrite after adsorbed by SIAX. C=S and C–O–C stretching vibration peaks are found in  $1027.89\text{ cm}^{-1}$  and  $1207.20\text{ cm}^{-1}$ , respectively. Analysis results of IR spectrum show that SIAX may absorb on auriferous pyrite surface in the form of chemical adsorption.

As shown in Fig. 9, stretching vibration peaks of C–H in  $2956.35\text{ cm}^{-1}$  and  $2869.72\text{ cm}^{-1}$  are found in the IR spectrum of auriferous pyrite after adsorbed by Y89. C=S and C–O–C stretching vibration peaks are found in  $1012.99\text{ cm}^{-1}$  and  $1267.20\text{ cm}^{-1}$ , respectively. Compared different spectrums in Fig. 9, stretching vibration peaks are much apparent, which indicate that collector Y89 can much strongly absorb on the surface of auriferous pyrite.

When the collector mixture of SIAX and Y89 was at a mass ratio of 1:2, the infrared spectral patterns of auriferous pyrite before and after interaction with mixed collector was studied. As shown in

Table 1

Chemical composition of the ore sample (mass fraction, %).

Composite	Au (g/t)	S	As	CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TFe
Grade	3.44	2.78	0.32	6.82	2.63	61.74	10.75	5.23

Table 2

Results of flotation tests performed on materials using pure and collector mixture.

Collector	Products	Yield/wt%	Au	
			Grade (g/t)	Recovery (%)
SIAX	Concentrate	19.94	12.77	74.03
	Tailings	80.06	1.12	25.97
	Feed	100.00	3.44	100.00
Y89	Concentrate	21.20	12.95	79.82
	Tailings	78.80	0.88	20.18
	Feed	100.00	3.44	100.00
SIAX:Y89 = 1:2	Concentrate	22.63	12.79	84.24
	Tailings	77.37	0.70	15.76
	Feed	100.00	3.44	100.00

Fig. 10, stretching vibration peaks of C–H in  $2955.78\text{ cm}^{-1}$  and  $2869.76\text{ cm}^{-1}$  are found in the IR spectrum of auriferous pyrite after adsorbed by mixed collector. C=S and C–O–C stretching vibration peaks are found in  $1016.73\text{ cm}^{-1}$  and  $1267.05\text{ cm}^{-1}$ , respectively. Compared spectra of Figs. 8–10, stretching vibration peaks have greater intensity in Fig. 10. It indicates that mixed collector can much strongly absorb on the surface of auriferous pyrite and improve the recovery of auriferous pyrite.

### 3.4. Flotation tests on materials

The materials containing auriferous pyrite in the flotation were obtained from Xinjiang, China. Chemical composition analysis was carried out X-ray fluorescence spectrometry (XRF) technique by using a Philips spectrometer. XRF results of the experiment sample are shown in Table 1.

Table 1 suggests that the main value elements in the materials is Au with a grade of  $3.44\text{ g/t}$ . And results of mineral characterization and chemical analysis indicate that Au mainly exists in auriferous pyrite, and quartz, sericite and dolomite are the dominate gangue minerals.

Based on the results of microflotation experiments, adsorption measurements and FI-IR analyses, the raw ore flotation tests were investigated under the condition of different collector. In raw ore flotation,  $500\text{ g}$  of sample was used for each test. Grinding fineness of feed was  $90\%$  passing  $74\text{ }\mu\text{m}$ . Type of flotation machine is XFD-1.5L and made in Changchun of China. The pH was adjusted to 9 with NaOH, and the dosage of terpenic oil was  $30\text{ g/t}$ . The results of the raw ore flotation experiments are listed in Table 2. When the collector mixture of SIAX and Y89 is at a mass ratio of 1:2, an Au concentrate assaying  $12.79\text{ g/t}$  Au is produced at a Au recovery of  $84.24\%$ . Comparing SIAX or Y89 as alone collector, the Au recovery has a significant improvement at the same reagent consumption. The 1:2 collector mixture SIAX + Y89 shows great potential for industrial application.

### 4. Conclusions

- (1) In this study, the flotation of fine auriferous pyrite was studied with a collector mixture of Sodium iso-amylxanthate (SIAX) and its isomeride (Y89). It can be noted that, when the two strong collectors were mixed for recovering auriferous pyrite, the higher recovery can be obtained than alone collector. There exist an optimal mass ratio between two collectors.

- (2) Adsorption measurements show that the adsorption density of collector on auriferous pyrite slightly decreases increasing pH from 4 to 9 and greatly decreases with from 9 to 12. Comparing to use collector alone, the mixed collector has greater adsorption density on the surface of auriferous pyrite under condition of the same collector concentration in the whole pH range.
- (3) The infrared spectral analysis suggests that mixed collector can much strongly absorb on the surface of auriferous pyrite, and the stretching vibration peaks have greater intensity. This is the reason that collector mixture can improve the recovery of auriferous pyrite. The collector mixture SIAX + Y89 exhibits great potential for industrial application in fine auriferous pyrite flotation.

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