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## FLOTATION SEPARATION OF WOLFRAMITE FROM QUARTZ USING N-OLEOYL SARCOSINE ACID AS COLLECTOR

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**Abstract:** In this study the collecting power of N-oleoyl sarcosine acid towards wolframite and quartz was studied using flotation. The adsorption mechanism was also discussed based on the results from adsorption experiments, zeta potential measurements and infrared spectroscopy study. The flotation results showed that N-oleoyl sarcosine acid showed a good collecting power towards wolframite, and the optimal flotation pH = 7 was obtained. However, the collecting power of N-oleoyl sarcosine acid towards quartz was weak. Therefore, the flotation separation of wolframite from quartz can be performed using N-oleoyl sarcosine acid as a collector. The adsorption tests and electrokinetic studies showed that N-oleoyl sarcosine acid adsorbed only on the wolframite surface. Additionally, the results from the infrared spectroscopy study confirmed that N-oleoyl sarcosine acid is adsorbed on the wolframite surface, and the metal complex (ferricarboxylate) maybe the major adsorbed species.

**Keywords:** *flotation, N-oleoyl sarcosine acid, wolframite, quartz*

### Introduction

Tungsten has a wide application in industry such as high temperature technology, chemical, lighting, X-ray technology, machine construction due to its low vapor pressure, high melting point, good electrical and thermal conductivities, high density, high elastic modulus, high wear resistance and good X-ray performance (Ilhan et al., 2013; Rao, 1996). It is one of the strategic metals identified for stockpiling in many countries. Meanwhile, wolframite is the principle mineral of tungsten and is often associated with other minerals such as quartz, calcite, fluorite, and apatite. Therefore,

wolframite must be separated from gangue minerals (Dawei et al., 1986; Marinakis and Kelsall, 1996).

The main beneficiation method of wolframite is gravity separation (Luo et al., 2013; Srivastava and Pathak, 2000). However, since the gravity separation is uncertain, flotation becomes an attractive alternative process (Deng et al., 2015; Hu et al., 1997; Srinivas et al., 2004). Therefore, searching for collectors for effective flotation of wolframite is highly desirable.

Oleoyl sarcosine is a commonly used collector for flotation of fluorite and siliceous scheelite ores (Celik et al., 1998; Hirva and Tikka, 2002; Ozcan et al., 1994; Ozcan O and Bulutcu, 1993). However, it has not been used in the flotation of wolframite. In the present study, the collecting abilities of the *N*-oleoyl sarcosine acid towards wolframite and quartz were studied through flotation tests. The adsorption mechanism was also discussed.

## Material and experimental

### Samples and reagents

Pure wolframite used for all experiments. It was obtained from a tungsten ore-dressing plant of Chongyi Country, Jiangxi province, China. A lump wolframite sample was firstly hand-crushed by a hammer, then removed from gangue minerals by high intensity magnetic separation. The obtained wolframite sample of 96.5% purity was then ground to  $-74\ \mu\text{m}$  with an agate mortar. The quartz sample was obtained from a tungsten ore-dressing plant in Ganzhou, Jiangxi province, China. It was hand-picked and ground to  $-74\ \mu\text{m}$ . Its purity was 99.9%.

Table 1. Chemical composition of wolframite and quartz (%)

Sample	WO <sub>3</sub>	Fe	Mn	SiO <sub>2</sub>	CaO
Wolframite	73.80	11.00	6.14	0.27	0.94
Quartz	-	-	-	99.9	-

*N*-oleoyl sarcosine acid, hydrochloric acid (HCl) and potassium hydroxide (KOH) were of analytical grade. Distilled water was used in all experiments.

## Experiments

### Micro-flotation experiment

The flotation tests of single minerals and artificially mixed minerals were performed. The mixture contained equal amounts of wolframite and quartz. The flotation tests were carried out in a mechanical agitation flotation machine equipped with a  $40\ \text{cm}^3$  cell. The impeller speed was fixed at 1900 rpm. The mineral suspension was prepared by adding 2 g of minerals to  $40\ \text{cm}^3$  of solutions. The pH of the mineral suspension was adjusted to a desired value by adding KOH or HCl stock solutions. The collectors

were added at a desired concentration and conditioned for 5 min. Then, flotation was carried out for a total of 4 min. The floated and unfloat particles were collected, filtered, and dried. The flotation recovery was calculated based on solid weight distributions between the two products. For mixed minerals flotation, the  $\text{WO}_3$  contents of the concentrates and tailings were determined by chemical analysis and the recovery was calculated.

### **Adsorption measurements**

For the adsorption tests, 1 g of mineral powder was added into 100 cm<sup>3</sup> N-oleoyl sarcosine acid solution at the desired concentration using a 250 cm<sup>3</sup> Erlenmeyer flask. The suspension was mixed using a rotator for 8 h, ensuring that the adsorption process reached equilibrium. Each sample was then centrifuged, and the residual concentration of N-oleoyl sarcosine acid in the solution was analyzed using the UV absorbance method.

### **Zeta potential measurements**

The zeta potential measurements of wolframite and quartz surfaces were carried out using a micro-electrophoresis technique. Potassium nitrate was used to maintain the ionic strength at  $1 \cdot 10^{-3}$  mol/dm<sup>3</sup>. Small amounts of the sample were added to desired amounts of solution and ultrasonicated for 3 min, magnetically stirred for 5 min. The pH of the suspension was adjusted using HCl or KOH. The zeta potential of sample was then measured using a JS94H micro-electrophoresis apparatus produced by Shanghai Zhongchen Digital Technique.

### **FTIR study**

The infrared spectra of wolframite before and after interacting with N-oleoyl sarcosine acid were recorded using a Nexus 670 Fourier Transform Infrared Spectrometer (FTIR) produced by Nicolet Instrument Corporation in the range of 4000–350 cm<sup>-1</sup>. Approximately 2 mg of the desired powder sample was thoroughly mixed with 200 mg of spectroscopic grade KBr and pressed into pellets for recording the spectrum.

## **Results and discussion**

### **Flotation separation of wolframite from quartz using N-oleoyl sarcosine acid as collector**

The effect of pH on the flotation performance of wolframite and quartz with N-oleoyl sarcosine acid as collector (100 mg/dm<sup>3</sup>) was investigated and the results are shown in Fig. 1. It can be seen from Fig. 1 that the optimal flotation pH for wolframite was 7 and the recovery of wolframite reached 86% at this pH. The results in Fig.1 also show that N-oleoyl sarcosine acid has a weak collecting power towards quartz and the recovery of quartz is always less than 10% over a wide pH range.

The effect of collector dosage on the flotation of wolframite and quartz was also studied at pH 7 and the results are shown in Fig. 2. It is evident from Fig. 2 that the

flotation recovery of wolframite increased from 49% to 94% with the increase of collector dosage from 10 mg/dm<sup>3</sup> to 150 mg/dm<sup>3</sup>. However, the recovery of quartz changed little with the increase of *N*-oleoyl sarcosine acid dosage.

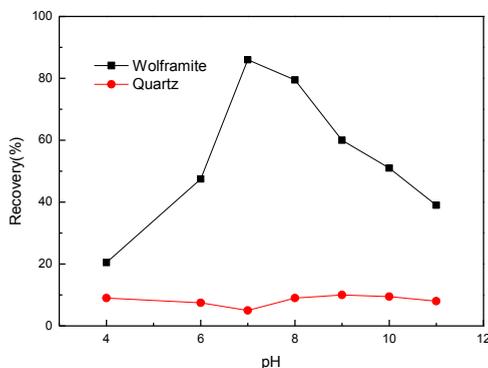


Fig. 1. Effect of pH on the flotation of wolframite and quartz

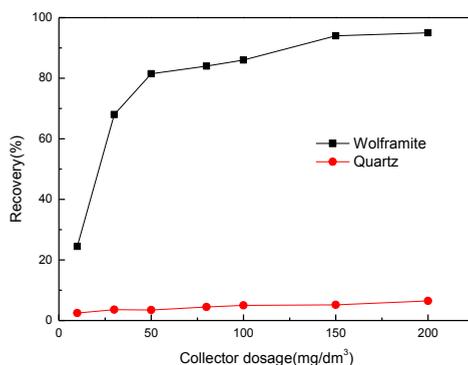


Fig. 2. Effect of collector dosage on the flotation of wolframite and quartz (pH = 7)

The flotation results suggest that it may be possible to float wolframite from quartz using *N*-oleoyl sarcosine acid as a collector. The results shown in Fig. 2. illustrate that a certain degree of selectivity was achieved using *N*-oleoyl sarcosine acid as the collector.

Table 2. Results of flotation separation of wolframite-quartz mixture at pH 7

Flotation Conditions	Products	Yield (%)	Grade (%)	Recovery (%)
N-oleoyl sarcosine acid 100 mg/dm <sup>3</sup>	Concentrate	38.3	68.7	71.3
	Tailings	61.7	17.2	28.7
	Feed	100.0	36.9	100.0

### Adsorption behavior of N-oleoyl sarcosine acid on wolframite and quartz

The adsorption of collector onto the mineral surface is an important parameter that affects the flotation response. The adsorption studies were carried out to probe the effect of pH and collector dosage on the adsorption density of the collector. The results are presented in Figs.3 and 4, respectively.

As shown in Fig.3, the adsorption capacity of N-oleoyl sarcosine acid on the wolframite surface first increased and then decreased with the increase of pH and the preferable pH range was basically in accordance with the optimum flotation pH. The result in Fig.3 also shows that N-oleoyl sarcosine acid is not adsorbed on the quartz surface. The results in Fig.4 show that the adsorption amount of N-oleoyl sarcosine acid on the wolframite surface increased with the increase of initial concentration while the adsorption amount of N-oleoyl sarcosine acid on the quartz surface showed no change.

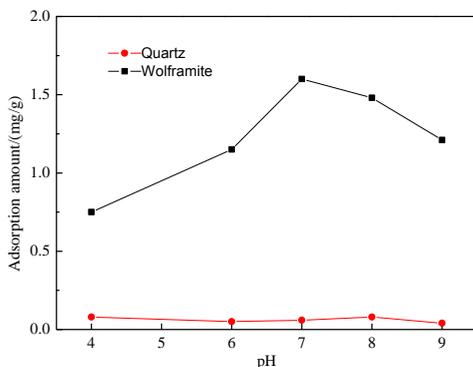


Fig. 3. Effect of pH on the adsorption of collector on wolframite and quartz

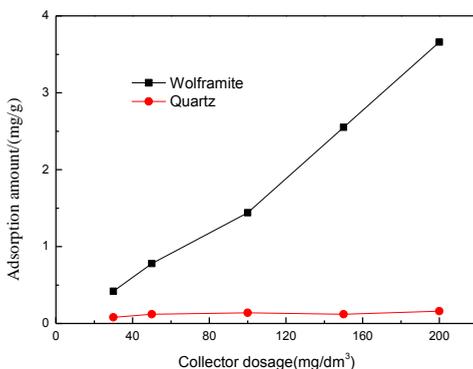


Fig. 4. Effect of collector dosage on the adsorption of collector (pH = 7)

### Adsorption mechanism of *N*-oleoyl sarcosine acid on wolframite surface

The electrokinetic studies for the wolframite and quartz particles as a function of pH are shown in Fig.5. It can be seen from Fig. 5 that the zeta potentials of wolframite and quartz are negative at all pH values. As seen from Fig. 5, the zeta potential of quartz is more negative than that of wolframite. After the addition of *N*-oleoyl sarcosine acid, the zeta potential of wolframite changed to more negative. Since both wolframite and *N*-oleoyl sarcosine acid were negatively charged, the adsorption of *N*-oleoyl sarcosine acid on the wolframite surface had to overcome the electrostatic repulsion, and the adsorption mechanism was not electrostatic adsorption. In contrast to wolframite, the zeta potential of quartz was not influenced by *N*-oleoyl sarcosine acid. This indicates that *N*-oleoyl sarcosine acid does not interact with the quartz surface.

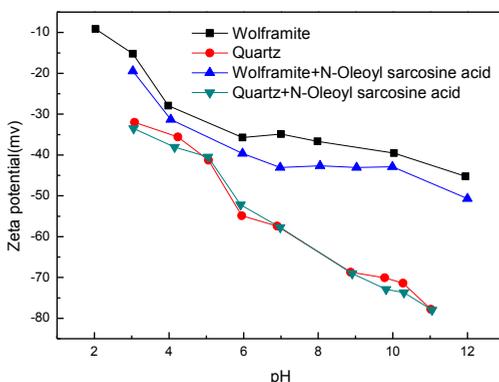


Fig. 5. Effect of *N*-oleoyl sarcosine acid on the zeta potential of wolframite and quartz

In order to study the adsorption mechanisms of *N*-oleoyl sarcosine acid on the wolframite surface, the infrared spectra of wolframite before and after interaction with *N*-oleoyl sarcosine acid at pH 7 were recorded and the results are shown in Fig. 6. The infrared spectrum of *N*-oleoyl sarcosine acid presented in Fig.6 (line c) shows peak at  $2922.57\text{ cm}^{-1}$  due to stretching vibration of C-H in  $\text{C-H}_2$ . The peak at  $2856.74\text{ cm}^{-1}$  is the symmetric stretching and asymmetric stretching of  $\text{C-H}_2$ . The peak at  $1634.48\text{ cm}^{-1}$  is the stretching vibration peaks of C-O in  $-\text{COOH}$  and  $1562.07\text{ cm}^{-1}$  is the stretching vibration peak of O-O in  $-\text{CON}$ . The infrared spectrum of wolframite (line a) shows peaks at  $811.60\text{ cm}^{-1}$  and  $612.67\text{ cm}^{-1}$  which are characteristic adsorption peaks of  $\text{WO}_4^{2-}$ . After the interaction with *N*-oleoyl sarcosine acid, the stretching vibration peaks of C-H at  $2921.13\text{ cm}^{-1}$  and  $2853.42\text{ cm}^{-1}$  were found in the spectrum of wolframite. The C-O stretching vibration peaks ( $1641.38\text{ cm}^{-1}$ ) were also found suggesting that *N*-oleoyl sarcosine acid is adsorbed on the wolframite surface.

The *N*-oleoyl sarcosine acid has the interacting polar carboxylate group and carbonyl group, which can participate in the interaction with the metal ion resulting in

a tridentate binding (Gordejev and Hirva, 1999). Thus, it can be concluded that N-oleoyl sarcosine acid was adsorbed on the wolframite surface through its two oxygen atoms in the carboxylate group and the carbonyl oxygen binding with metal atoms on wolframite surface.

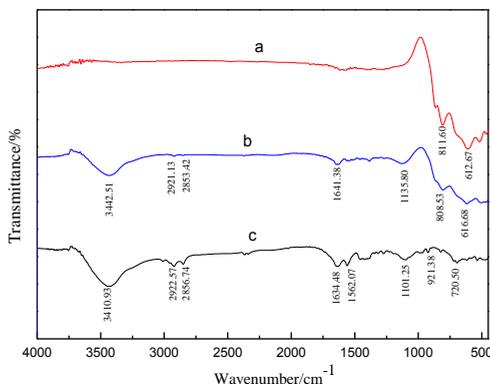


Fig. 6. Infrared spectrum in the absence and presence of N-oleoyl sarcosine acid (a – wolframite, b – wolframite after interacted with N-oleoyl sarcosine acid, c – N-oleoyl sarcosine acid)

## Conclusions

The collecting power of N-oleoyl sarcosine acid towards wolframite and quartz was investigated and the adsorption mechanism was discussed. The following conclusions can be drawn from the above observations.

A good flotation performance was observed when N-oleoyl sarcosine acid was used as a collector for wolframite flotation in the pH range of 6 to 8 and the optimum pH value was found around 7.

The N-oleoyl sarcosine acid has weak collecting power towards quartz. It provides effective separation between wolframite and quartz without any depressant.

The adsorption of N-oleoyl sarcosine acid occurred on the wolframite surface through a chemical adsorption and the metal complex maybe the major adsorbed species.

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