SYNERGISM OF WOLFRAMITE FLOTATION WITH BENZYL ARSONIC ACID AND SODIUM BUTYL XANTHATE①

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ABSTRACT

Wolframite flotation with benzyl arsonic acid and sodium butyl xanthate is studied, at first. It shows the efficiency of mineral processig is good when the two agents are added together. Then the synergism of sodium butyl xanthate and benzyl arsonic acid is studied also by HPLC.

Keywords: HPLC synergism wolframite benzyl arsonic acid sodium butyl xanthate

1 INTRODUCTION

Wolframite flotation with benzyl arsonic acid has been used in industry for a long time[1], and when sodium butyl xanthate was added as a subsidiary collector, the consumption of expensive benzyl arsonic acid could be decreased and the efficiency of agent could be improved. In addition, the synergism of flotation agents has been cared by many investigators[2,3], a lot of compositions have been tested in industry production[4,5]. However, the action of synergism can only be guessed[2] for lack of favourable analytical method. In this paper, HPLC is used as a way of quantitative analysis to determine the synergism of the two collectors.

2 FLOTATION EXPERIMENT

2.1 *Reagents, Minerals and Flotation Procedures*

Commercial grade benzyl arsonic acid (BAA) was used as one of the collectors in this study after purification by twice recrystalization from warm water; It was titrated by sodium hydroxide to get a final concentration of 3.96×10^{-2}mol / L.

Commercial grade sodium butyl xanthate (SBX) was used as a subsidiary collector after purification by multiple recrystallization from acetone; its final concentration of solution was 2.74×10^{-2}mol / L.

Wolframite containing 71.71 wt−% WO_3 was −200 meshin size.

The pH was adjusted using NaOH and H_2SO_4 solutions which concentrations were 0.5 mol / L.

Flotation tests were conducted using a flotation machine with hanging fillister. Two grams of the mineral were used in each tests. The mineral suspension was stirred for 1 , 2, 6 and 1 min respectively after addition of water, Pb^{2+} ion, collector and $2^{\#}$ oil. The flotation time was 3 min.

①Manuscript received December 25, 1991

2.2 *Flotation Experiment*

All flotations were carried out according with orthogonal experiments design (Table 1).

Table 1 Research for signficance factor and level

factors	A	B	C	D
levels	BAA / 10^{-3} mol · L^{-1}	SBX / 10^{-3} mol · L^{-1}	Pb^{2+} / 10^{-3} mol · L^{-1}	pH
1	1.58	0.55	0.64	2
2	4.75	1.10	1.44	4
3	7.92	5.48	2.62	6

The results show the effect of sodium butyl xanthate, benzyl arsonic acid and pH to recovery is bigger than that of Pb^{2+} ion. In the meantime, higher collector concentration has bigger recovery rate; pH 4 is the best condition of pH. Hence, pH was fixed to 4.50 ± 0.2 in the subsequent experiment; The quantity of Pb^{2+} ion was fixed to 2.2 mL.

To research the effect of order that collectors were added, orthogonal experiment was set up according to Table 2. Here sodium butyl xanthate is added at first, flotation procedures were just the same as above, but $2^{\#}$ oil is added at the 9 th min.

Table 2 The factors and levels when sodium butyl xanthate was added at first

level	factor		
	B(SBX) / 10^{-3} mol · L^{-1}	A(BAA) / 10^{-3} mol · L^{-1}	E($2^{\#}$ oil) / mg · L^{-1}
1	1.10	B × 50 vol–%	88.8
2	3.29	B × 100 vol–%	177.6

The experimental results show that the synergism of sodium butyl xathate and benzyl arsonic acid has considerable effect on the flotation recovery rate. But the average recovery rate is only 54.01%, the reason may be that sodium butyl xanthate of being added at first had decreased the adsorption of benzyl arsonic acid on the surface of mineral. So hereafter the experiment will be done by being added arsonic acid at first below (see Table3, 4).

Table 4 shows A_1B_1 is the best combination, A_2B_1 is the second one. It means that the effect of volume ratio of agents 2:1 is better than 1:1.

We did also orthogonal experiment below to decide which ratio is better, 3:1 or 2:1?

From Table 5 and using A × B to express the effect of synergism. We can get the Table 6 below.

In table 6, $A_1B_2 > A_1B_1$, $A_2B_2 > A_2B_1$. This indicates that the volume ratio of collectors 2:1 is better than 3:1.

Table 3 The factors and levels when benzyl arsonic acid was added at first

levels	factor		
	A(BAA) / 10^{-3} mol · L^{-1}	B(SBX) / 10^{-3} mol · L^{-1}	E($2^{\#}$ oil) / mol · L^{-1}
1	1.58	A × 50 vol–%	88.8
2	4.75	A × 100 vol–%	177.6

Table 4 Research for A × B

factors	B_1	B_2
A_1	87.72	78.67
A_2	86.05	66.18

Table 5 The factors and levels for researching the better ratio of collectors

levels	factor		
	A(BAA) / 10^{-3} mol · L^{-1}	B(SBX) / 10^{-3} mol · L^{-1}	C(Pb^{2+}) / mg · L^{-1}
1	0.95	A × 1 / 3 (volume ratio)	1.44
2	1.88	A × 1 / 2 (volume ratio)	2.66

Table 6 Research results for A × B

factors	B_1	B_2
A_1	58.18	62.76
A_2	67.03	90.05

All the wolframite flotation tests with sodium butyl xanthate and benzyl arsonic acid show that the best pH is 4.50 ± 0.2, the concentration of Pb^{2+} has no effect when the concentration of collectors is not very low. In all

experiments, the synergism of sodium butyl xan- thate and benzyl arsonic acid has bigger effect on the recovery rate of wolframite. The action of synergism is the strongest when the volume ratio of SBX and BAA is 2:1, the molar rario is 2.89:1. When benzyl arsonic acid is 291.1 mg / L and sodium butyl xanthate is 94.7 mg / L, the recovery rate of wolframite is above 90%. According to the reference [1], benzyl arsonic acid must be 1,500 mg / L when benzyl arsonic acid is used alone. A great quantity of collectors can be saved due to the synergism of agents.

3 HIGHER-PERFORMANCE LIQUID CHROMATOGRAPHIC(HPLC) AND ITS APPLICATION

3.1 *Instrument and Method*

In order to research the synergism of collectors the adsorption of sodium butyl xanthate and benzyl arsonic acid must be determined. Generally we may use UV spectrophotometric method to determine the UV absorption of agents, however after sodium butyl xanthate has been oxided to dixanthate, the UV absorptions are still overlap. Therefore the HPLC instrument BT8100, made in Germany, was used to separate and determine the agents.

3.2 *Analytical conditions of the HPLC*

In the experiment, mobile phase is methanal and water. The peak shape of benzyl arsonic acid is fine when the ratio of methanal to water is 90:10, the flow rate is 1.0 ml / min, the wave-length of UV is at 235 nm. When we research the analytical condition of sodium butyl xanthate, we find that the peak shape is not fine at any conditions. After sodium is oxided to butyl dixanthate (BDX), the best analytical condition of benzyl arsonic acid (BAA) make the peak shape of BDX good. Thus we get the retention time for BAA about 1.400 min, for BDX 9. 100 min. We can determine the mixture of the two collectors. The results are shown in Fig. 1.

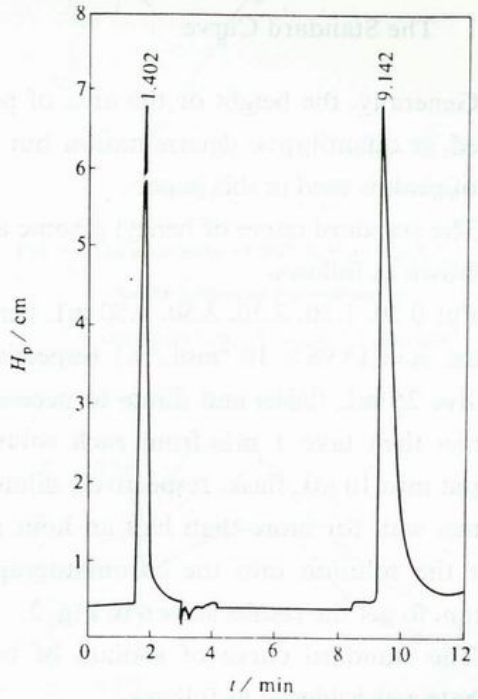

Fig. 1 The retention time of BDX and BAA

Hp——peak height; *t*——retantion time

3.3 *The Adsorption of* Pb^{2+} on the Surface of Mineral

After Pb^{2+} is added into the solution as activator, the Pb^{2+} which exists in the solution and on the surface of mineral must affect the adsorption of the collectors. Therefore, we must research the adsorption of Pb^{2+}. The atomic absorption spectrometer was used to determine the Pb^{2+}.

After Pb^{2+} is added to the mineral suspension and stirred 1 min, the adsorption of Pb^{2+} reaches 95.35%; and after 2 min reaches 98.21%. After we use the Ac^- to reach with

Pb^{2+}, the increment of Pb^{2+} in the suspension is less than 1%. Therefore the effect of Pb^{2+} will be deducted in our experiment.

3.4 *The Quantitative Analysis of the Synergism of Collectors on the Surface of Wolframite*

3.4.1 The Standard Curve

Generally, the height or the area of peak is used in quantitative determination but the area of peak is used in this paper.

The standard curve of benzyl arsonic acid was drawn as follows:

Put 0.50, 1.50, 2.50, 3.50, 4.50 mL benzyl arsonic acid (3.96×10^{-2}mol / L) respectively into five 25 mL flasks and dilute to necessary volume; then take 1 mL from each solution and put into 10 mL flask, respectively dilute to volume, wait for more than half an hour and inject the solution into the chromatographic column, to get the results shown in Fig. 2.

The standard curve of sodium of butyl xanthate was achieved as follows:

Take 1.00, 2.00, 3.00, 4.00, 5.00, 6.00 mL

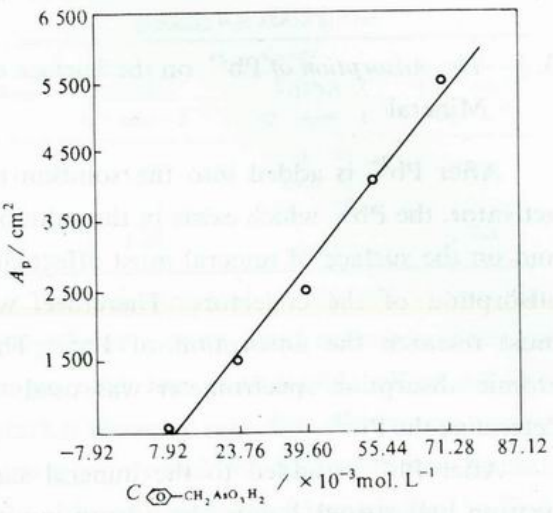

Fig. 2 The standard curve of BAA($\bigcirc-CH_3AsO_3H_2$)

C—concentration; A_p—peak area

2.74×10^{-2}mol / L sodium butyl xanthate and put into six 25 mL flasks and dilute to the necessary volumerespectively; then take 1 mL from each of the above solutions put into six 10 mL flasks and add iodide into each flask untill the color of solution becomes yellow, finally dilute to necessary volume with methanol and inject the solution into the chromatographic column for measuring and getting Fig. 3.

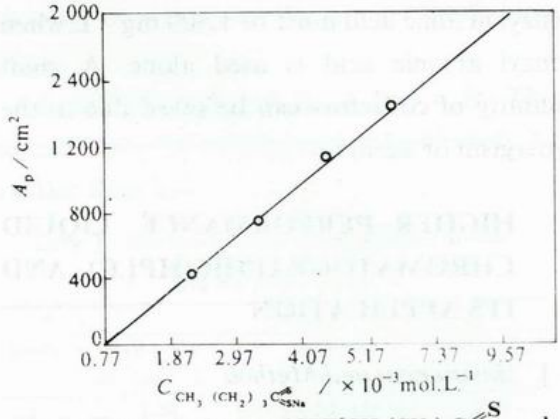

Fig. 3 The standard curve of SBX[$CH_3(CH_2)_3C(=S)SNa$]

A_p—peak area; C—concentration

3.4.2 The Adsorption of Collectors and the Synergism of Collectors in the Different Conditions

(1) The adsorption of benzyl arsonic acid (BAA, $\bigcirc-CH_2AsO_3H_2$),

Weigh wolframite 2.000 g, put it into the flotation groove, add water until the general volume approaches to 25.00 mL, stir 1 min, add Pb^{2+} 2.2 mL (1.64×10^{-2}mol / L), stir 2 min. The result shows in Fig. 4. Curve 1, only add benzyl arsonic acid and stir 7 min; curve 2, add benzyl arsonic acid at first and stir 1 min, then add sodium butyl xanthate and stir 6 min; curve 3, add sodium butyl xanthate at first and stir 1 min, then add benzyl arsonic acid and stir 6 min. Fig. 5 shows the adsorption of benzyl arsonic acid on the surface of mineral.

The adsorption of sodium butyl xanthate

(SBX, $CH_3(CH_2)_3C\overset{S}{\underset{SNa}{=}}$).

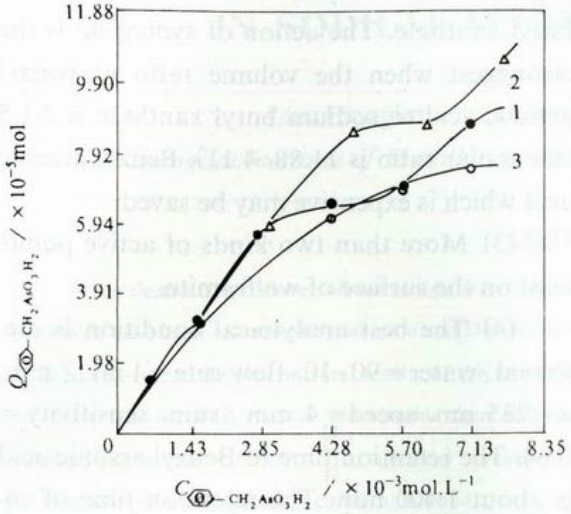

Fig. 4 The adsorption of BAA($\langle O\rangle-CH_2AsO_3H_2$) on the surface of 2 g wolframite under different concentration of BAA

C—concentration; *Q*—quantity absorped

(2) The procedure of adding sodium butyl xanthate is just the same as benzyl arsonic acid. The ability of adsorption of sodium butyl xanthate on the surface of mineral is very strong. The curve of adsorption is shown in Fig. 5. Whether benzyl arsonic acid is added or not, the adsorption of sodium butyl xanthate has no change.

(3) The synergism of benzyl arsonic acid and sodium butyl xanthate

After changing the concentration of sodium butyl xanthate, we can get the curve of adsorption for benzyl arsonic acid (3 mL 3.96 × 10^{-2}mol / L) on the surface of 2 g wolframite as Fig. 6, Curve 1 shows the effect of sodium butyl xanthate added at first; curve 2, benzyl arsonic acid added at first. The procedure is just the same as above.

In Fig. 4, the adsorption curve of benzyl arsonic acid appears the greater slope after it

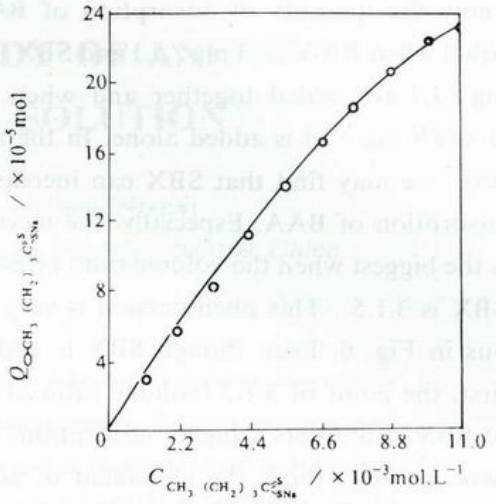

Fig. 5 The adsorption of SBX [$CH_3(CH_2)_3C\overset{S}{\underset{SNa}{=}}$] on the surface of 2 g wolframite

C—concentration; *Q*—quantity absorped

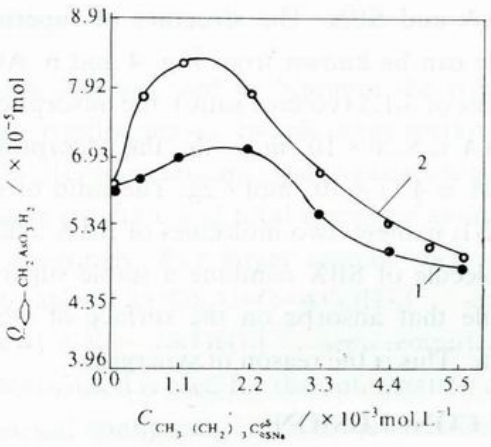

Fig. 6 The adsorption of BAA($\langle O\rangle-CH_2AsO_3H_2$) (Q) on the surface of 2 g Wolframite under differennt concentration (c) of BAA($\langle O\rangle-CH_2AsO_3H_2$)

appears a flat. It indicates that the surface of wolframite exists more than two kinds of active adsorption points. One of these points has more energy and can adsorb agents easily. The other kind has less energy, it can adsorb agents only when the concentration of agents is bigger;At the same time, it can also adsorb agents easily when the synergism exists between the agents. Comparing curve 1 with curve 2, we

know the quantity of adsorption of BAA is equal when BAA (873 mg / L) and SBX (284.2 mg / L) are added together and when BAA (1,454.9 mg / L) is added alone. In the meantime, we may find that SBX can increase the adsorption of BAA. Especially, the increment is the biggest when the volume ratio of BAA to SBX is 3:1.5 . This phenomenon is very obvious in Fig. 6. Even though SBX is added at first, the point of 3:1.5 (volume ratio of BAA to SBX) still exists a bigger adsorption. From here, we may think the increment of adsorption and the improvement of recovery rate are not caused by the active point of wolframite; We may think also that a kind of supermolecule has formed between the molecules of BAA and SBX. The structure of supermolecule can be known from Fig. 4 and 6. At the point of 3:1.5 (volume ratio), the adsorption of BAA is 8.26×10^{-5}mol / 2g, the adsorption of SBX is 4.11×10^{-5}mol / 2g. The ratio of mole is 2:1, namely, two molecules of BAA and one molecule of SBX combine a stable supermolecule that adsorbs on the surface of wolframite. This is the reason of synergism.

4 CONCLUSION

(1) HPLC is a good method to research the mechanism of flotation with more than one collector. The method is not only accurate and reliable, but also quick and covenient;

(2) The synergism exists in the wolframite flotation with benzyl arsonic acid and sodium butyl xanthate. The action of synergism is the stronggest when the volume ratio of benzyl arsonic acid to sodium butyl xanthate is 3:1.5 (the molar ratio is 11.88: 4.11). Benzyl arsonic acid which is expensive may be saved;

(3) More than two kinds of active points exist on the surface of wolframite;

(4) The best analytiacal condition is methanal : water = 90 : 10, flow-rate = 1 mL / min, $\lambda = 235$ nm, speed = 4 mm / min, sensitivity = 0.64; The retention time of Benzyl arsonic acid is about 1.400 min; The retention time of sodium butyl xanthate is about 9.100 min;

(5) The synergism chiefly causes by the supermolecule between Benzyl arsonic acid and sodium butyl xanthate. The molar ratio is 2 : 1.

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