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## Peculiarities of the Joint Use of Apolar Sulphur-Containing Reagent and Sulphydryl Collector in Flotation of Gold-Bearing Pyrite

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### Abstract

The effect of an apolar reagent, sulphur-aromatic concentrate (SAC), and its composition with potassium butyl xanthate (PBX) on flotation and sorption properties of gold-containing pyrite was investigated. Mineral fractions with grain sizes of  $-0.074+0.044$  and  $-0.044+0.02$  mm with pyrite mass fraction of 91.8 and 92.2 %, and gold contents of 50.5 and 54.5 g/t, correspondingly, were used for flotation experiments. Experiments were carried out in a microflotation device in the presence of T-80 foaming agent. It was determined that SAC had the collecting ability against samples of pyrite with different particle sizes, however, its activity was lower compared to that of PBX. It was demonstrated that pyrite fraction flotation response under effects of PBX and SAC reduced with decreasing mineral grain sizes. In flotation of pyrite with grain sizes of  $-0.074+0.044$  and  $-0.044+0.02$  mm, a flow rate reduction of PBX up to 50 % is likely with its use in composition with SAC without recovery loss. During flotation of pyrite thin fraction, PBX/SAC composition (25 % SAC fraction of PBX flow rate) facilitated an increased pyrite recovery degree into the froth product by 5 %. The treatment of the mineral of a size of  $-0.074+0.044$  mm with an aqueous emulsion of SAC results in its sorption, by which its collecting ability of pyrite may be explained. The nature of sorption is probably physical, as SAC partially passes into the water during subsequent washings. At the same time, the presence of SAC on the mineral surface facilitates PBX sorption and hence its flow rate during flotation, which is consistent with the findings.

**Keywords:** gold-containing pyrite, sulphur-aromatic concentrate, butyl xanthate, flotation, sorption

### INTRODUCTION

Against the depletion of stream gold reserves and the involvement of lode gold into the processing, the issue of efficient recovery of gold-bearing minerals from ore raw materials becomes relevant. The main part of noble metals, including gold, for the majority of hydrothermal fields is concentrated as inclusions in sulphide minerals, in a greater degree, in pyrite [1] that may float using sulphydryl collecting agents [2]. The use of compositions of sulphydryl reagents-collecting agents with different activity and ionogenicity,

and also additional reductants, including apolar ones, creates favourable conditions for selective flotation of pyrites of various modifications [3–6].

As demonstrated in [7], the apolar reagent, *i.e.* sulphur-aromatic concentrate (SAC), in composition with potassium butyl xanthate (PBX) is efficient during flotation gold recovery from gravity circuit tailings (95 %,  $-0.074$  mm grade), whereat a part of gold is linked with sulphide minerals (pyrite and arsenopyrite). The use of SAC and PBX compositions in the optimum ratio facilitates increased gold recovery degree and improved concentrates quality, and also reduced consump-

tion of sulphhydryl collector. Herewith, high-sulphur oil fractions, from which SAC is obtained, are hardly suitable for usual processing and are considered as undesirable oil product components.

When apolar reagents and heteropolar collecting agents are jointly used the strength of adhesion of mineral particles to the bubble increases significantly, which allows increasing the upper size limit of floated particles [8]. On the other hand, the introduction of organic additives to the flotation process may enhance selective flocculation caused by adsorption of anion collecting agents and thereby generate optimal conditions for flotation of such particles [9]. It is noted in [10, 11] that a reactant sorbed physically facilitates the elimination of kinetic limitations preventing the formation of flotation contact, namely, removing a water layer between the mineral particle and the air bubble.

The present work investigated the efficacy of SAC in composition with PBX during flotation of gold-containing pyrite with different particle sizes and its effect on adsorption of the main reactant-collector.

## MATERIALS AND METHODS

Sulphur-aromatic concentrate was produced at the Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences (IPC SB RAS, Tomsk) from high-sulphur oil fractions by two-stage extraction with a solution of zinc chloride in *N,N*-dimethylformamide. The concen-

trate is a water-insoluble liquid and is used as a relatively water-stable emulsion produced by dispersing using the UV disperser. The composition of SAC was explored by HPLC and GC-MS methods and represented a mixture of aromatic hydrocarbon (48.5 %) and organosulphur compounds (51.5 %), composed of mono-, bi-, and tricyclic structures [7], and was notable for high sulphur content including sulphide (3.7 %).

Pyrite was selected according to characteristic features from the gravitational concentrate obtained during the enrichment of an ore sample from the Sukhoi Log deposit.

Crystalline forms of pyrite from the Sukhoi Log deposit, often in combination with less developed faces of other simple forms, are characterized by the primary development of cube faces. Throughout the mass of pyrite, gold is sporadically met, mainly as microscopic and thin inclusions. Almost the total gold of the deposit is enclosed precisely in pyrite [12].

Pyrite fractions with particle sizes of  $-0.074+0.044$  and  $-0.044+0.02$  mm were prepared for flotation experiments from crystals with a particle size of  $-2+1$  mm (Fig. 1). As demonstrated by analysis of the DSC thermogram (Netzsch STA 449 Jupiter) of pyrite crystals, the resulting thermal effects are consistent with literature data for pyrite [13].

The mineral and elemental compositions of the fractions were explored by X-ray fluorescence (X'Pert HighScore). The gold mass fraction was determined by assay-atomic-absorption. Pyrite is

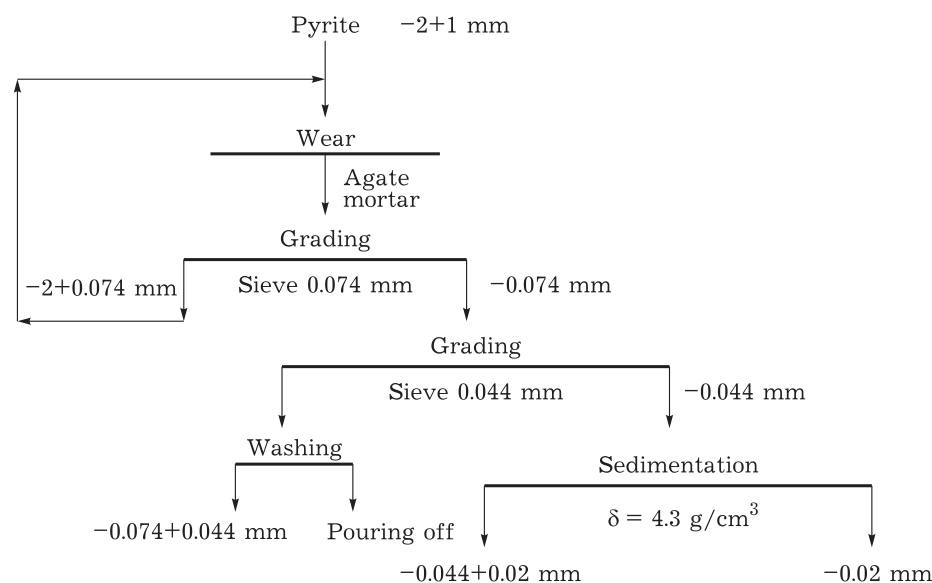


Fig. 1. Scheme for preparation of different pyrite size fractions.

TABLE 1

Phase composition of fractions under examination

Formula	Mineral	Mass fraction, %	
		Fraction, mm	
		-0.074+0.044	-0.044+0.02
FeS <sub>2</sub>	Pyrite	91.8	92.2
Ca(CO <sub>3</sub> )	Calcite	0.8	0.9
Fe <sub>1-x</sub> S	Pyrrhotite	0.8	0.8
Fe(CO <sub>3</sub> )	Siderite	1.3	2.1
SiO <sub>2</sub>	Quartz	5.1	3.9

prevailing in both fractions, according to X-Ray Fluorescence analysis (XRF). Impurity minerals are presented by pyrrhotite, siderite, calcite, and quartz (Table. 1). The fractions are slightly different in the content of the main elements (Table. 2). Apart from gold and aluminium, the presence of such mineral phases like arsenopyrite, chalcopyrite, pentlandite, and aluminosilicates is likely.

The data acquired in the exploration of the mineral composition of the fractions using scanning electron microscopy (TM-1000 and TM-3000 equipped with an X-ray spectral analyzer), testify the presence of gold with content as high as 0.1 % in pyrite. Native gold with a size in 30  $\mu\text{m}$  was recorded in pyrite (Fig. 2).

Flotation experiments were carried out in a microflotation apparatus, its design being proposed in [14].

An experimental plant involved a 16 cm<sup>3</sup> flotation chamber composed of two section-coupled portions. Air from the microcompressor entered the lower portion of the chamber through a glass filter. The mixing of the mineral (0.5 g) with reagents was carried out in the lower portion of the chamber with S/L = 1 : 10 in a volume of 5.0 mL using a magnetic stirrer (400 min<sup>-1</sup>). Flotation was carried out in distilled water. The effect of PBX and SAC on flotation results was explored in the presence of T-80 foaming agent (1.0 mg/g). Reagents such as PBX and T-80 were fed into the process as solutions (concentration 0.05 %), SEC – in the form of an aqueous emulsion (0.05 % concentrations). The contact time with T-80, PBX, and SAC is 1 min. After mixing with the reagents, the lower portion of the chamber was connected to the upper one and filled with distilled water. Afterwards, the system was fed with air; its constant flow rate was monitored by a pressure gauge. The air flow rate was set experimentally for a flotation time of 3 min. The experiments were carried out 22 °C.

TABLE 2

Elemental composition of the studied fractions

Element	Mass fraction, %	
	Fraction, mm	
	-0.074+0.044	-0.044+0.02
Gold	50.5	38.1
Arsenic	0.52	0.51
Copper	0.14	0.22
Nickel	0.13	0.14
Cobalt	0.09	0.10
Aluminium	0.18	0.70
Silicon	2.27	2.47
Calcium	0.17	0.12

Research on sorption of PBX and SAC reagents with pyrite was performed by UV spectroscopy (Shimadzu UV-300 and Camspec 500 spectrophotometers) of liquid phases before and after contact of aqueous solutions of the reagents and their mixtures with mineral surface according to typical absorption maxima. Spectra of PBX were compared according to the known maximum in the region of 301 nm. An aqueous emulsion of SAC has a typical spectrum in the 200–350 nm range; spectra of SAC in ethanol and hexane solutions were recorded in a similar area. Mineral samples (1.0 g) were selected from a freshly prepared fraction of pyrite with a size of -0.074+0.044 mm, wetted with water, and stirred using a magnetic stirrer with a solution of PBX or an aqueous emulsion of SAC for 5 min. In order to determine the effect of SAC on sorption of PBX, the mineral was sequentially treated with the former, rinsed with water, and then treated with a solution of the latter. Liquid phases were centrifuged, decanted, and subjected to spectrophotometry in the UV spectral range.

## RESULTS AND DISCUSSION

### *Microflotation of pyrite with different particle sizes using BAC and PBX*

Table 3 gives experimental results on the flotation of samples of pyrite with different particle sizes without collectors. It can be seen that a fraction of -0.044+0.002 mm, a thinner material, has enhanced flotation activity under natural conditions (without reagents). When a foaming agent is introduced into the process (at constant flow rate) the picture changes. The larger fraction (-0.074+0.044 mm) has a greater degree of the recovery. That does not contradict classical

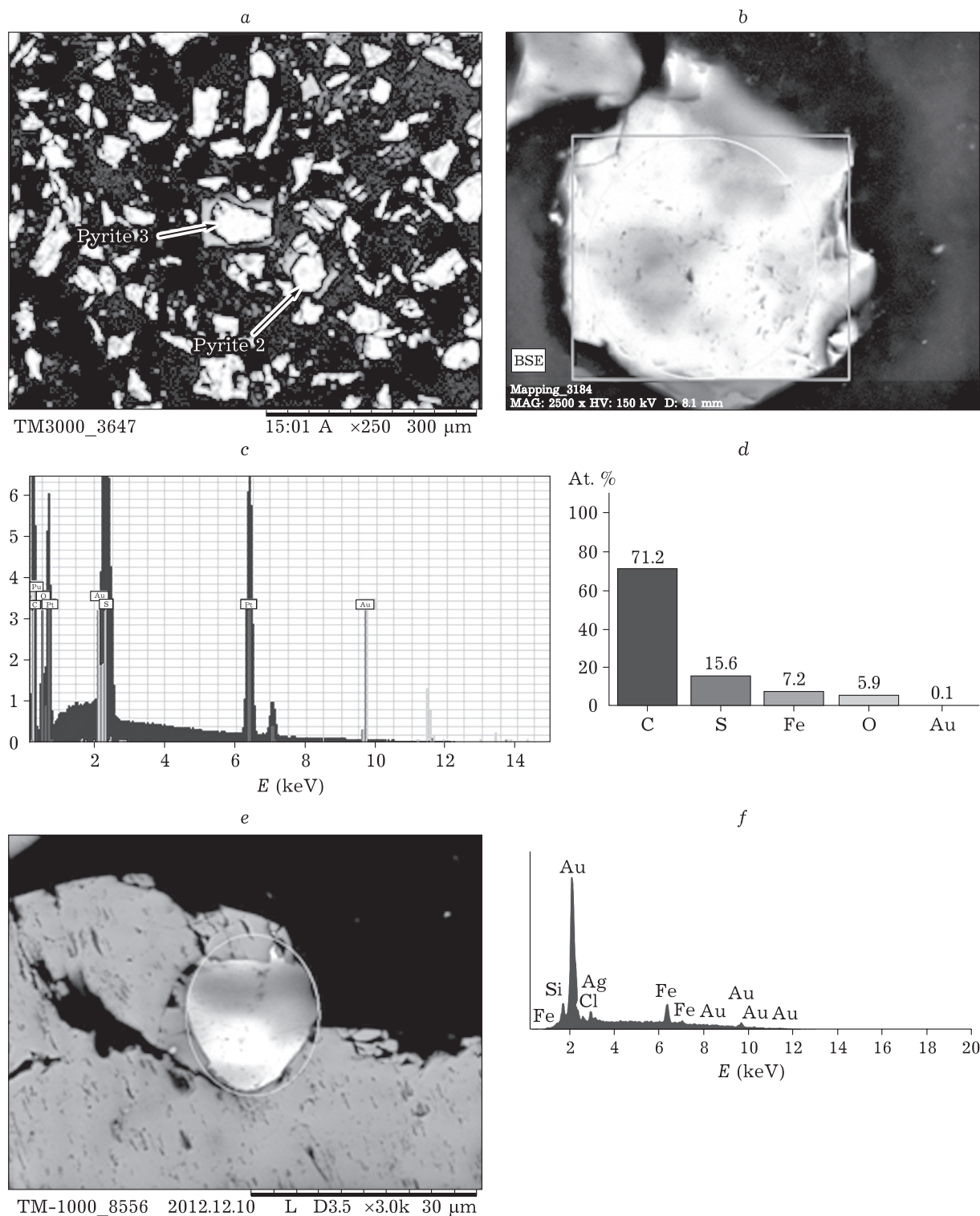


Fig. 2. Micrographs of pyrite present in a fraction with a size of  $-0.044+0.02$  mm at different magnifications (a, b) with total XRD pattern of the indicated scanning area (c) and elemental composition diagram (d); e, f – micrograph and XRD pattern native gold in pyrite, respectively.

concepts regarding the function of sizes of the mineral grains under flotation conditions [9].

Figure 3 demonstrates the effect of the flow rates of PBX and SAC on the photoactivity of

samples of pyrite with different particle sizes. It can be seen that BAC has greater collecting ability towards the tested samples than PBX. When PBX and BAC are separately used for flotation



of fractions with a size of  $-0.074+0.044$  and  $-0.044+0.002$  mm, differences in the degree of recovery are 10.7 и 13.8 %, respectively.

Table 4 and Fig. 4 give experimental results on the combined use of SAC and PBX in different ratios with optimum collector flow rates. It can be seen (Fig. 4) that due to this, one may reduce the flow rate of the main reactant-collector in compositions as high as 50 % without recovery loss.

The uses of PBX in composition with SAC with a portion of the latter as high as 25 % is accompanied by a recovery increase up to 5.0 %. A further increase in SAC fraction and hence a decrease in the flow rate of the main reactant-collector results in recovery reduction. A fraction of SAC as high as 50 % when using it in composition with PBX in the flotation of pyrite with a size of  $-0.044+0.002$  mm may be considered critical.

**Research on sorption of PBX and SAC on pyrite**

Numerous research works are devoted to investigating the mechanism of sorption of xanthogenates on sulphide minerals. It is known that the interaction of PBX with pyrite, like with the majority of sulphide minerals, is accompanied by PBX oxidation to mainly form dixanthogenide [15–17]. Oxidation on pyrite turns out to be most significant.

Our results on the interaction of PBX with gold-containing pyrite are consistent with literature data. When the initial concentration of PBX is from 10 to 90 mg/L after its contact with the aqueous phase, there is no adsorption band with a maximum near 301 nm. Herewith, the spectrum of an alcohol solution acquired by mineral surface wash after contact with PBX corresponds to the known one of dixanthogenide with typical adsorption bands at 240–285 nm. Beginning with an initial concentration of 90 mg/L for PBX, there is a typical band with a maximum at 301 nm in the liquid phase. In all likelihood, PBX mainly turns into dixanthogenide, as pyrite actively catalyzes the oxidation of xanthogenate.

TABLE 3

Flotability of samples of pyrite with different particle sizes without collecting agents

Flotation conditions	Recovery, %	
	Fraction, mm	
	$-0.074+0.044$	$-0.044+0.02$
Distilled water	6.6	15.6
Same + T-80	39.0	26.0

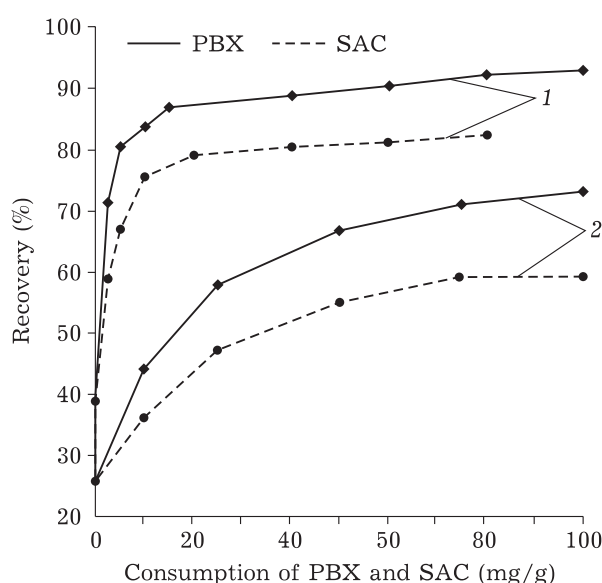


Fig. 3. Recovery of pyrite with a size of  $-0.074+0.044$  mm (1) and  $-0.044+0.02$  mm (2) versus PBX and SAC consumption.

Spectra of an aqueous emulsion of sulphur-aromatic concentrate (curve 1) and SAC in hexane (curve 2) and alcohol (curve 3) solutions differ in the 220–300 nm absorption region (Fig. 5). Spectra of SAC in alcohol and hexane solutions have more intense and narrow absorption bands, which is related to higher solubility of mixture components in  $C_2H_5OH$  and  $C_6H_{14}$ . There is even a greater difference in spectra after contact of SAC with the mineral. As can be seen from Fig. 6 data, optical density values of absorption bands in the 220–300 nm region are significantly reduced in the UV spectrum of an aqueous emulsion of SAC compared to those in the initial emulsion

TABLE 4

Effect of SAC amount PBX/SAC composition on recovery of fractions of pyrite with different particle sizes

Total consumption, mg/g (SAC fraction, %)	Recovery, %
<b>Fraction <math>-0.074+0.044</math> mm</b>	
0.8 (0)	92.0
0.8 (20)	92.0
0.8 (50)	92.6
0.8 (75)	88.0
<b>Fraction <math>-0.044+0.02</math> mm</b>	
1.0 (0)	73.0
1.0 (10)	76.0
1.0 (25)	78.0
1.0 (50)	76.5
1.0 (75)	72.6
1.0 (90)	67.0

(curve 1), which testifies partial sorption of SAC on the mineral surface.

After contact with the mineral surface, there is also an expansion of absorption bands and their displacement towards short waves of in spectra of the SAC emulsion. This change in the spec-

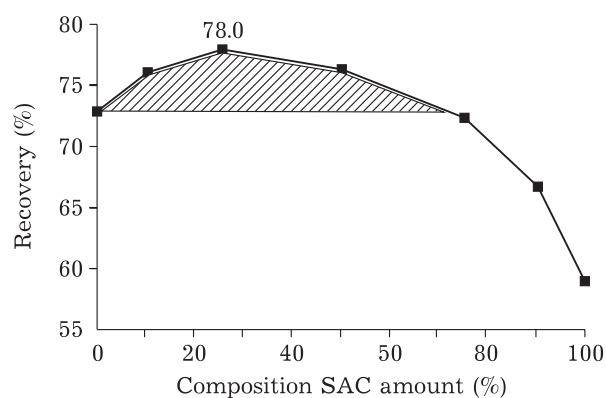


Fig. 4. Effect of SAC amount in PBX/SAC composition on recovery of pyrite with a size of  $-0.044+0.02$  mm (total consumption of 1.0 mg/g).

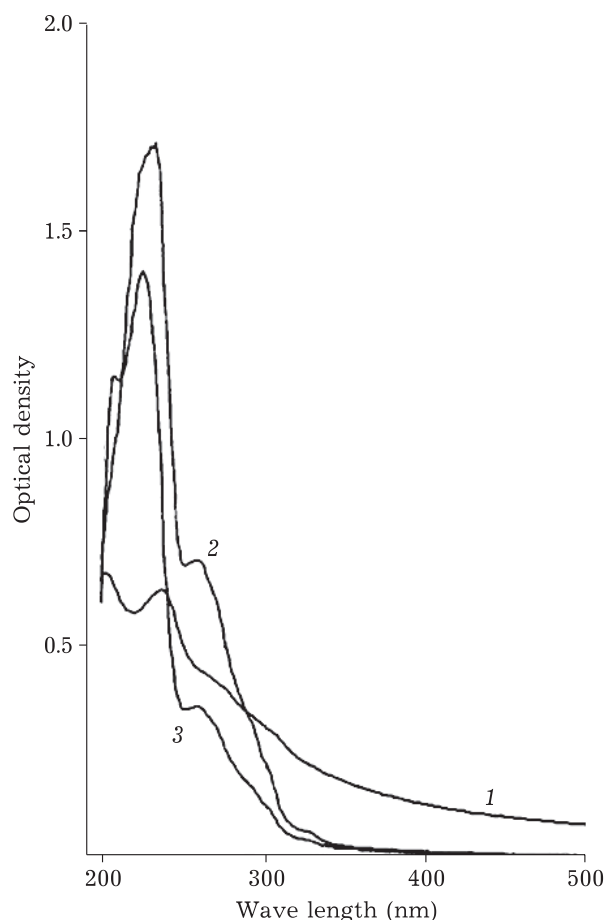


Fig. 5. UV spectra of SAC ( $C = 20$  mg/L): 1 is aqueous SAC emulsion, 2 is hexane SAC solution, 3 is ethanol SAC solution.

trum may be explained by the unequal sorption of various compounds that are part of SAC. During washings of the surface of the treated mineral with water, SAC partly passes into water. However, UV spectra of washings from the mineral surface (curve 3) also significantly change, as sorption and desorption of the reactant that is a mixture complex by composition proceed in a different manner.

As demonstrated by the results acquired during sequential treatment of the mineral with SAC emulsion and PBX solution, the residual concentration of PBX in the aqueous phase in this case substantially increases compared to that without treatment with SAC. Table 5 demonstrates the residual concentration of PBX in the liquid phase after treatment of pyrite with potassium butyl xanthate only and pre-treatment with SAC upon content of 60 mg/L of the latter in the emulsion.

As can be seen from Table 5 data, the residual concentration of PBX in the solution is 7.5 mg/L (with its initial content of 60 mg/L) during pre-treatment with SAC, whereas there are trace amounts therein after contact with the mineral only with its initial concentration of 90 mg/L. Stirring the solution with the mineral at higher

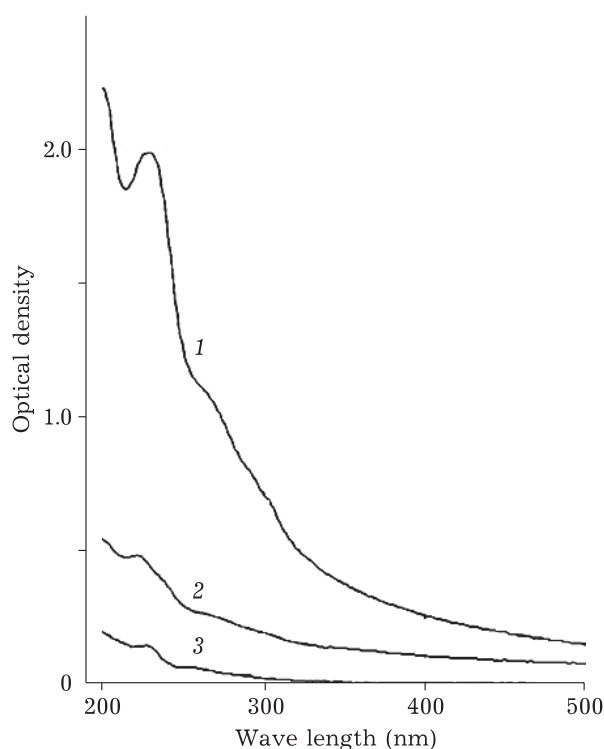


Fig. 6. UV spectra of SAC emulsion ( $C = 60$  mg/L): 1 is the initial emulsion, 2 is the emulsion after pyrite surface treatment, 3 is wash-off from pyrite surface after treatment with SAC emulsion.

TABLE 5

Residual PBX concentration in a solution versus pyrite surface treatment method (SAC emulsion content of 60 mg/L)

Initial PBX concentration, mg/L	Residual PBX concentration, mg/L	
	Without pre-treatment of pyrite	With pre-treatment by SAC emulsion
10	0	0
30	0	5.2
60	0	7.5
90	0.34	25.7
120	1.71	34.2
150	6.18	45.9

concentrations of PBX (150 and 200 mg/L) does not lead to the complete removal of the xanthogenate therefrom, therefore there are residual amounts of potassium butyl xanthate in spectra of these solutions. In that manner, pyrite surface treatment with an emulsion of SAC results in its sorption on the mineral surface and thereby in PBX flow rate reduction.

## CONCLUSION

Resulting from the research undertaken, it has been determined that the collecting ability of sulphur-aromatic concentrate (SAC) during flotation of gold-containing pyrite of different sizes is lower than that of potassium butyl xanthate (PBX). Photoactivity of pyrite under the effects of both PBX and SAC is decreased from a larger fraction of pyrite to the thinner one. The use of SAC in composition with PBX during flotation of pyrite with a particle size from  $-0.074$  to  $0.02$  nm makes it possible to reduce sulphhydryl collector consumption as high as 50 % without production data reduction. During flotation of gold-containing pyrite with a particle size of  $-0.044+0.02$  mm, PBX flow rate reduction as high as 25 % with enhanced recovery up to 5.0 % is likely due to SAC.

Pre-treatment of the mineral with an emulsion of SAC results in its sorption on the mineral surface; however, when further washed, it partly passes to water. Herewith, UV spectra of washings from the mineral surface are changed, as sorption and adsorption of the reactant that is a mixture complex by composition proceed in a different manner. Nevertheless, the presence of SAC in the surface proves to be sufficient for reduced PBX sorption value. Thereby SAC may facilitate PBX flow rate reduction during flotation, which is consistent with the findings on the flotation of gold-containing pyrite. At the same time, the

presence of sorption of sulphur-aromatic concentrate on the mineral may explain the ability of SAC to float pyrite independently.

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