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Technical Note

Interaction of butyl xanthate with oxidized surface of sphalerite

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ABSTRACT

The rate constants for the reaction of potassium butyl xanthate (PBX) and copper sulphate with the surface of natural sphalerite have been determined by the method of spectrophotometry. It is shown that the decrease of the reaction rate has been caused by blocking the mineral surface by the reaction products which resulted in decreasing the amount of the formed dixanthogen and flotation activity of sphalerite. The rate of oxidizing decomposition of xanthate-anion on the oxidized sphalerite surface does not depend on the presence of elementary sulphur on it and increases in presence of active surface copper cations. elementary sulfur forms on the oxidized surface of sphalerite represented as separate phases and is not an inert substance in respect to flotation reagents due to the formation of steady matter of the type of copper sulphides CuS_n ($n \geq 1$), which was not active in respect to xanthates.

Keywords: Flotation; Sphalerite; Butyl xanthate; UV-spectroscopy

1. INTRODUCTION

As a result of contact with water and air oxygen the surface of sulphide mineral is subjected to oxidation (Mitrofanov 1958; Abramov *et al.*, 1975; Mielczarski *et al.*, 1995). According to (Glazunov, 1980; Eliseev *et al.*, 1984; Avdokhin and Abramov, 1989) oxidation of mineral surface occurs to form elementary sulphur. It is shown (Oko, 1975) that sulphur is formed in contact of the mineral sulphide surface with air on grinding, which is proved, for example, by the oxidation of sphalerite samples from the deposit "Zhairem" (Podvishenskii and Bondarenko, 1987). The content of elementary sulphur formed as a result of oxidation on crushing of pyrite, chalcopyrite and sphalerite has been quantitatively determined (Boriskov *et al.*, 1984). It has been shown (Glazunov, 1991), that up to 1,4 apparent monolayers of elementary sulfur are formed on the sphalerite surface on oxidation, whereas 4.7, 2.1 and 1.7 monolayers are formed on pyrite, galena and chalcopyrite, respectively. Last minerals are subjected to faster oxidation. Oxidation kinetics of the sphalerite particle surface was investigated (Kuzina *et al.*, 1999) and the presence of two stages of this process was detected: fast stage, caused by oxidation of the first monolayer, and slower stage, associated with a diffusion through the oxidized surface layer. The basic product of oxidation in these conditions is elementary sulphur. The catalyst of sphalerite oxidation is the impurity ions of transition metals.

Thus, the new solid phase - elementary sulphur is formed on the sulphide mineral surface prepared to flotation. It is noted (Eliseev *et al.*, 1984; Glazunov, 1999) that sulphur has an effect on the flotation of sulphide minerals, but the action of sulphur is ambiguous: sulphur activates, for example, the process of chalcopyrite flotation, depressing pyrite flotation (Glembotskii and Klassen, 1973) and has insignificant effect on the activity of sphalerite flotation (Boriskov *et al.*, 1986).

Sphalerite flotation is substantially defined by the ratio of technologically active substances formed in the flotation system on the basis of xanthate and salts of copper (II). There are open questions on the interaction of these reagents with elementary sulfur and its influence on the rate of their transformation and fixing on the mineral surface.

The purpose of the present work is to study the kinetics features of interaction of potassium butyl xanthate (PBX) solutions and copper sulphate with the oxidized surface of sphalerite during flotation of zinc and to establish the influence of surface elementary sulfur on the character of these interactions.

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2. EXPERIMENTAL

2.1. Materials

The investigations were carried out using crystals of natural sphalerite. The content of basic and impure metals in the mineral was: Zn - 59.010 %, Fe - 5.370 %, Pb - 0.075 %. Proper iron phases were not found by the method of XRD analysis. A specific surface of sphalerite particles of various sizes was measured by the BET method on argon absorption. The value of specific surface for a fraction by the size of 20 microns was 1.1m^2/g; for a fraction of -0.1+0.02mm it was equal 0.1m^2/g.

2.2. Equipment and experimental procedure

Definition of elementary sulfur formed on the surface of sphalerite particles was carried out by the method of extraction by the organic solvent followed by the method of spectrophotometry. The kinetics of interaction of the PBX and Cu(II) cations with the sphalerite surface was studied using a technique described in (Okolovich and Figurkova, 1977; Kosikov *et al.,* 1986) by continuous running of solutions through a layer of a sphalerite sample with constant rate. Determination of the reagent amount absorbed by the surface was carried out on a residual concentration of the reagent after passing of the solution through a mineral layer. Each consecutive portion by volume of 5sm^3 was selected as an appropriate test number after running of a reagent solution. By the results of measuring the residual reagent concentration, test average values of rate constants of the interaction of PBX and copper sulfate with the sphalerite surface were calculated in approximation of the pseudo-first order reaction.

Desorption of water-insoluble products from the sphalerite surface was carried out by the method of extraction by ethyl alcohol. The concentration of dixanthogen and elementary sulfur in these extracts were determined by the method of spectrophotometry. The concentrations of xanthate anions, elementary sulfur and dixanthogen in the solutions were determined by the intensity of characteristic bands with λ_{max}= 298nm, λ_{max}= 262nm and λ_{max}= 285nm, respectively. The concentration of Cu^{2+} in the solution was determined by the technique (Mukhina *et al.,* 1965) using Bismuthol-II reagent.

The VIS and UV absorption spectra were registered by the spectrophotometer "Shimadzu" UV-300.

3. RESULTS AND DISCUSSION

3.1. Condition of the sphalerite surface

Sphalerite samples are subjected to oxidation, which under ambient conditions proceeds according to the following scheme:

$$Fe^{2+} \text{ (near to the surface)} + k/2\ O_2 \rightarrow Fe^{3+} + (O_k)^- \quad (1)$$

$$k \cdot ZnS + (O_k)^- \rightarrow k \cdot ZnO + (S_k)^- \quad (2)$$

$$2(S_k)^- \rightarrow S^{2-} + S^0_{2k-1} \quad (3)$$

where k = 1, 2

One of the main reasons of oxidation of the sphalerite surface is the presence of iron in the natural zinc sulfide (Kuzina *et al.,* 1999). The rate of oxidation is directly proportional to the contents Fe^{2+} in the sphalerite samples.

With the formation of an oxidized film with the thickness of about a monolayer, the oxidation of the surface of natural sphalerite practically stops, which testifies that a limiting stage of process (2) is diffusion of sulfide-anions to the surface of a sample.

3.2. Interaction of the collector with the initial sphalerite surface

The average reaction rate constants (K) of the reagent with the sphalerite surface are given in Table 1. The reaction rate of PBX with the oxidized surface of zinc sulfide non-activated by the Cu^{2+} cations is rather high in the initial tests, when the surface is free from the reaction products. When the degree of the surface covering increases the rate is reduced and is not dependent on the presence of free elementary sulfur. It specifies that during oxidation of the sulfide mineral the distribution of sulfur formed on the sphalerite surface is non-uniform (elementary sulfur is in the form of particles of its own phases).

The UV-spectra of the extraction products from the sphalerite surface are recorded with the purpose of identification of the reaction products. The absorption bands from organic compounds formed as a result of decomposition of PBX on the oxidized zinc sulfide are observed in the studied spectra (Figure 1). In accordance with the data (Leonov and Kolmogortsev, 1969; Khan *et al.,* 1986) the decomposition proceeds according to the complex mechanism, forming various products, for example, sulphocarbonates CS_3^{2-}, COS^{2-}, CS^{2-}, monothiocarboxylic acids, the most typical of which is dixanthogen.

The study of stability of water solutions of xanthate shows, that the main stage of PBX decomposition is oxidizing destruction. The products of oxidation of PBX perform as catalysts for PBX disintegration due to the formation of intermediate complexes with molecular oxygen. The sharp increase of a decomposition rate of PBX-anion after its partial oxidation proves such a phenomenon. The proof of participation of intermediate active particles is the independence of PBX decomposition rate of its concentration. The oxidized surface of the mineral is the reason of PBX destruction on this surface due to the presence of the active forms of oxygen and transition metals (equation 1-3).

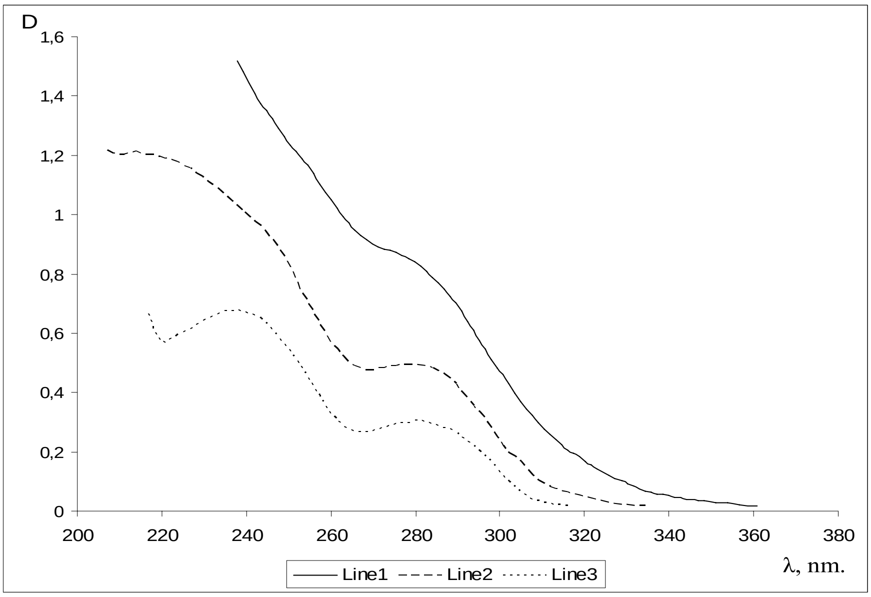

Figure 1. Spectra of extraction products of a sphalerite treated by PBX: 1- sulfur is removed from the sphalerite surface; 2- without removal of sulfur

Similar investigations of PBX interaction with the oxidized sphalerite surface are carried out on samples previously processed by a solution of copper sulfate (Table 1).

Table 1
The reaction rate constants of PBX with the oxidized sphalerite surface

Number of consecutive test	Reaction rate constants of PBX with oxidized sphalerite surface, $1/m^{2}*c^{-1}$			
	The sphalerite sample is not activated by copper sulphate		The sphalerite sample is activated by copper sulphate	
	An initial sample	Sulfur is removed from the sphalerite surface	An initial sample	Sulfur is removed from the sphalerite surface
1	0.62	0.67	*	*
2	0.19	0.22	*	1.04
3	0.12	0.10	0.84	0.92
4	0.09	0.05	0.71	0.49
5	0.07	0.05	0.73	0.46
6	0.05	0.05	0.60	0.43
7	0.03	0.05	0.42	0.42
8	0.03	0.05	0.25	0.44

*Constants for these tests were not determined because of a very low residual reagent concentration.

It has been shown that the values of the rate constants of the reaction of xanthate-anion with the sphalerite surface previously treated by $CuSO_4$ increase in contrast to the samples not activated by copper sulfate. This phenomenon is explained by the interaction of PBX with copper cations, therefore the amount of the reacted collector with these samples is several times higher in comparison with initial one. In Figure 2 the spectral characteristics of organic products extracted by ethyl alcohol from the sphalerite surface are given.

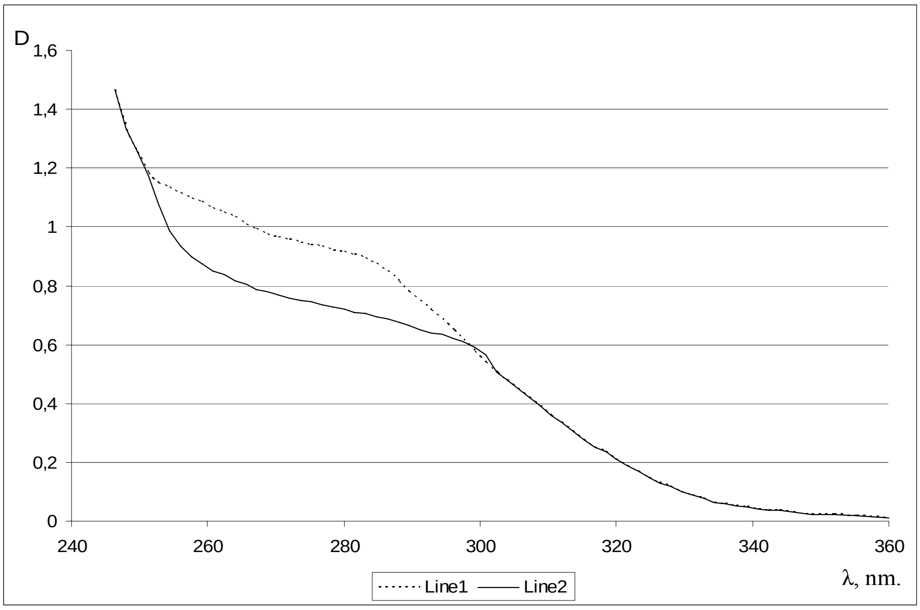

Figure 2. Spectra of extraction products of a sphalerite, treated by PBX and Cu^{2+}: 1 - sulfur is not removed from the sphalerite surface; 2 - sulfur is removed from the sphalerite surface; 3 - spectrum of dixanthogen

The spectrum of an organic phase from the sample previously washed from elementary sulfur (curve 2) is almost similar to the spectrum of dixanthogen (curve 3). One can see in Figure 2 that there is no complete coincidence between the spectrum for pure dixanthogen and the spectrum of the sample where the elementary sulfur was not extracted from the surface (curve 1). At the same time, absorption bands remained after separation of absorption bands peculiar to dixanthogen in the UV-spectrum are not characteristic for the spectrum of elementary sulfur. It is a consequence of interaction of sulfur with copper hydroxide present in the solution (pH of zinc flotation > 10), according to the following scheme:

$2Cu^{2+} + 3OH^{-} + 4S^{0} \rightarrow 2CuS + S_2O_3^{2-} + 3H^{+}$ (4)

Intermediate products of the specified reaction are copper polysulphides. In the presence of xanthate-anions the process of interaction of elementary sulfur is supplemented by the reaction:

$Cu^{2+} + 2ROCSS^{-} + S^{0} \rightarrow CuS + (ROCS_2)_2$ (5)

In alkaline solutions the elementary sulfur cooperates with cations of Cu^{2+} forming copper sulphides and polysulphides, which form surface complexes with xanthate-anions. Therefore, for samples, where S is not removed from the surface, the amount of the reacted xanthate-anions is reduced 1,5 times in comparison with the samples where sulfur is removed (Table 1).

The calculated amount of dixanthogen, formed on the sphalerite surface after extraction of elementary sulfur by ethyl alcohol was 44% in comparison with 30% without preliminary removal of sulfur. The quantity of chemically fixed xanthate by Cu^{2+} cations on the surface after extraction of elementary sulfur was estimated as 56%. Thus, for samples without sulfur the reaction with active copper cations makes the main contribution to process of xanthate-anions interaction:

$2Cu^{2+} + 4ROCSS^{-} \rightarrow 2Cu^{1+}\,ROCSS^{-} + (ROCS_2)_2$ (6)

On the oxidized sphalerite surface containing elementary sulfur the formation of a stable compound CuS_n ($n \geq 1$) occurs according to reaction (4). Therefore, with the subsequent treatment by xanthate-anion the formation of dixanthogen by reaction (6) is impossible for some part of copper. The formation of CuS_n according to the scheme (4) explains higher rate constants of the reaction of copper cations with the sphalerite surface in the initial period at the presence of elementary sulfur (Table 2). Further on, the formed surface CuS_n compound blocks an active surface of the mineral, which leads to a decrease of the reaction rate constant.

A series of experiments on the study of interaction of the surface with a PBX solution were carried out with the purpose of estimation of the efficiency of PBX transformation in dixanthogen on sphalerite, where elementary sulfur was previously removed from surface and treated by Cu^{2+} cations (Table 3). The amount of PBX transformed to dixanthogen was determined as 68%, 52%, 53%, respectively at 1, 2, 3 consecutive treatments. Thus, the reaction of xanthate-anion with the surface proceeds mainly according to reaction (6) with the formation of a complex of copper xanthate and dixanthogen.

Table 2
The rate constants of the reaction of copper sulphate with the sphalerite surface

Number of test	A rate constant of reaction of Cu^{2+} with a sphalerite surface, $1/m^2 \cdot c^{-1}$	
	The initial sample	Sulfur is removed from the sphalerite surface
1	*	0.88
2	0.73	0.56
3	0.49	0.47
4	0.34	0.44
5	0.24	0.37
6	0.10	0.32
7	0.08	0.24
8	0.05	0.14

* The definition of a rate constant for this test was not this possible due to a very low residual concentration of reagent

Table 3
The amount of PBX reacted with the sphalerite surface free from elementary sulfur and treated by Cu^{2+} cations

Test No.	Residual PBX amount in a solution, mol*10^{-6}	PBX amount, mol* 10^{-6}			PBX share, %	
		absorbed by a surface	expended on dixanthogen formation	chemically reacted	transformed in dixanthogen	chemically fixed on the surface
1	0	2.0	1.36	0.64	68	32
2	1.08	0.91	0.46	0.47	52	43
3	1.31	0.61	0.32	0.37	53	40

Similar investigations carried out on sphalerite samples containing elementary sulfur have shown that the reaction of PBX on equation (6) proceeds less effectively (only 36% of xanthate-anion transforms to dixanthogen).

It confirms the conclusion that copper cations lose their activity in relation to xanthate-anion due to the reaction of sulfur with copper hydroxide. The UV-spectra of the extraction products from the sphalerite surface treated by PBX are given in Figure 2: for the samples without preliminary removal of sulphur (curve 1) and for the samples where the sulfur was removed from the surface (curve 2). One can see in the Figure 2 that the main extraction product from the samples with removed sulfur is dixanthogen (curve 3). Under such conditions the process of flotation sphalerite proceeds successfully. In the case of the sphalerite samples where sulfur was not removed from the surface the contribution of dixanthogen is appreciably less (curve 1).

Therefore, the reduction of flotation activity of the mineral has been observed with the increase of elementary sulfur concentration on the surface of sphalerite (for strong oxidized samples, the content of Fe^{2+} > 10%) that was confirmed by the results (Podvishenskii and Bondarenko, 1987).

4. CONCLUSIONS

Elementary sulfur formed on the oxidized surface of sphalerite represented as separate phase and was not inert substance in respect to flotation reagents due to the formation of copper sulphides, which were not active in respect to xanthate.

It was established that the formation of elementary sulfur influences the character of interaction of xanthate-anion with Cu^{2+} cation on the oxidized surface of sphalerite and the composition of products. The apparent constants of the reactions have been estimated and it was shown that the reduction of the reaction rate was caused by blocking the mineral surface by reaction products which resulted in the decrease of amount of the formed dixanthogen and flotation activity of sphalerite. Hence, the presence of elementary sulfur on the sphalerite surface results in a change of interaction patterns of flotation reagents (potassium butyl xanthate and copper sulphate) with the surface and does not promote a hydrophobization of the mineral surface.

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