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Adsorption and flotation of copper sulfide ore with diisopropyldithiophosphate collector

Abstract: One of the topical problems of the enrichment industry is the evaluation of the influence of pulp chemistry on the sorption and flotation properties of sodium diisopropyl dithiophosphate. The affinity of the collector with respect to copper ore by the method of static sorption and flotation tests has been studied in this paper. The results of investigation adsorption mechanism of diisopropyldithiophosphate collector on the surface of the sulfide copper ore and flotation has been discussed. The investigation of composition and structure of sulphide copper ore has been carried out by using FT-IR-spectroscopy, X-ray diffraction spectroscopy and ICP-MS method. Based on the results of the analysis, the main minerals of copper ore, chalcocite and bornite, were selected. Also the analytical expressions of the real solubility constants of chalcocite and bornite, which connect the product of the solubility of hydroxocompounds at the phase interface with the solubility of copper diisopropyldithiophosphates and the oxidation-reduction ability of minerals, were obtained taking into account that the results showed that sorption capacity of ore at pH 10.5-11.5 is a maximum. The role of the oxidation-reduction processes in fixing of diisopropyldithiophosphate ion on the surface of ore was established. It was shown that data of extraction of copper to concentrate and adsorption value of diisopropyldithiophosphate ion are correlating. The IR-Fourier spectroscopic analysis showed that collector is coordinated with the ions of the metal of the crystal lattice of copper-containing minerals through the sulfur atoms of the dithiophosphate group.

Key words: sulfide copper ore; diisopropyldithiophosphate; adsorption; pulp chemistry; flotation.

Introduction

The polymetallic raw materials currently being processed are characterized by a fine dissemination of minerals and complex structural characteristics that make the flotation process more difficult. The diameter of the characteristic minerals – chalcosine, covellin, bornite in the copper sulfide ore varies: 0.2 mm for chalcosine and to 0.03 μm for bornite. The chalcocite inclusions have equigranular structure [1]. Theoretical substantiations and experimentally confirmed optimal conditions for flotation enrichment processes of sulfide polymetallic ores are the basis for creating innovative flotation technologies and ensuring the efficiency and complexity of mineral raw materials. The provision of an optimal reagent enrichment regime is referred to the problems that need to be solved, namely, the influence of the composition of copper ore and flotation reagents on the process of its processing [2-9], and the features of the flotation agent fixing mechanism on the mineral surface [10-13]. The purpose of this work is to study the flotation behavior of sulfide copper ore using sodium diisopropyldithiophosphate as a collector, to study the structure and composition of the ore and their effect on the interaction between collector and ore.

Materials and methods

Materials and reagents. Sulfide copper ore was obtained from a copper mine in Central Kazakhstan. The samples were wet-ground and elutriated. Size fractions were ±0.074 mm. The sodium diisopropyldithiophosphate (the content of pure substance is 78%) was prepared in a laboratory by diluting to a concentration of $4.25 \cdot 10^{-5}$ M and used as a main collector. Flotation reagent Oksal T-92 (mixture of polyhydric alcohols, aqueous solution) was used as a foam-forming agent (concentration $1 \cdot 10^{-5}$ M). The sodium hydroxide (1 M) and hydrochloric acid (1 M) of analytical purity were used as pH adjusters.

Distilled water was used in all experimental studies.

Adsorption tests. The amount of adsorbed collector on the ore was measured by potentiometric titration of the collector solution after the separation of the solid phase by the solution of copper (II) sulfate, Cu_2S was used as the indicator electrode [14]. 1 g of ore was immersed into 50 ml of an aqueous solution, containing the main collector ($4.25 \cdot 10^{-5}$ M) at a fixed pH for 30 min at 25°C. After that, the sample was centrifuged for 10 min at a rate of 9000 rpm/min.

Flotation tests. Flotation tests for sulfide copper ore were conducted by using a laboratory FML-1 (237 AK) flotation machine with cell (volume of 0.5 L). 100 grams of a copper ore were firstly mixed with 0.5 L distillate water in the flotation cell for 1 min with an impeller speed of 2000 rpm/min. The sodium hydroxide (1 M) or hydrochloric acid (1 M) was added to adjust the pulp pH to a predetermined pH. Collecting reagent and foam-forming agent were then added and conditioned for 8 min. The pulp pH was then adjusted slightly before flotation and was assumed to be the slurry pH at the end of flotation. The total flotation time was 9 min, and the concentrates were collected by manually scraping. Both the concentrates collected and the tailings remaining in the cell were dried and weighed for calculating flotation recoveries. All recovery results presented are the average of duplicate flotation tests.

Characterization. FT-IR spectroscopic measurements were carried out by the device FSM 1201. X-ray diffraction spectroscopy (XRD) spectra of samples of initial ore and concentrates were carried out by the X-ray powder diffraction D8 Advance (Bruker, Germany) with the Cu-k_α line of 0.15406 nm. ICP-MS study of elemental composition of sulfide copper ore was carried out by the spectrometer ICP MS Agilent 7500.

Results and discussion

Investigation of composition and structure of ore. The chemical composition of sulfide copper ore was determined for its description. Quantitative data on the content of chemical elements of rock-forming minerals were obtained by the method of inductively coupled plasma mass spectrometry (ICP-MS). Approximate values were obtained from the average of five test sites of each sample from heterogeneous rock materials. The results of the ore analysis are presented in Table 1.

Table 1 – Elemental composition of sulfide copper ore by results of chemical analysis

Element	Amount, %	Element	Amount, $g \cdot t^{-1}$	Element	Amount, $g \cdot t^{-1}$
Cu	1.99	Au	<0.01	La	26.90
Pb	0.04	Ag	15.02	Ce	55.82
Zn	0.01	Be	1.50	Pr	6.69
S	0.58	Sc	17.80	Nd	26.50
		Ti	5938.10	Sm	5.20
		V	146.35	Eu	1.50
		Cr	83.10	Gd	4.80
		Co	25.40	Tb	0.74
		Ni	68.59	Dy	4.20
		Rb	21.80	Ho	0.83
		Sr	558.70	Er	2.20
		Y	18.83	Tm	0.32
		Zr	171.30	Yb	2.10
		Nb	12.90	Lu	0.31
		Cd	1.90	Hf	4.60
		Cs	0.86	Pb	11.30
				Th	6.62
				U	2.10

The results of the chemical analysis show that the average copper content in the ore is 1.99%, and accordingly refers to the average. Besides copper, lead and zinc, the ore contains a relatively large amount of titanium, strontium, vanadium, zirconium. The presence of scattered elements was found in the sample. It also shows that ore contains lanthanides and actinides in a total amount of 162.73 $g{\cdot}t^{-1}$. Table 2 contains data on the mineralogical composition of sulfide copper ore.

Table 2 – Mineral composition of sulfide copper ore

Mineral (-s)	Mass fraction, %	Mineral (-s)	Mass fraction, %
Feldspar	65.71	Pyroxene	Rare grains
Chlorites	19.12	Azurite	
Quartz	7.82	Pyrite	
Calcite	0.85	Galena	
Epidotes	0.34	Magnetite	
Hematite	1.74	Covellite	
Bornite	1.01	Chalcopyrite	
Chalcocite	1.69	Iron hydroxides	
Malachite	0.09	Rutile, anatase	
Apatite	0.95	Zircon	
Totally	95.88		

It can be seen that rock-forming minerals are represented in the ore as feldspars, chlorites and quartz. Sulfide copper is presented in the form of chalcocite (1.69%) and bornite (1.01%), in the form of rare grains there are covellite and chalcopyrite.

Copper is represented by 13.57% of oxides and 84.92% of secondary sulfides, on 0.50% of primary sulfides. Sulfide copper ores consist mainly of ore minerals (containing 5.48%), rock-forming minerals (quartz, feldspar, chlorite and epidotes) with a content of 93.84%. Phase analysis was performed to establish the copper phases (Table 3) [15].

The main mass of copper is concentrated in sulfide form (85.43%), which in turn is divided into primary sulfides (0.50%) and secondary copper sulfides (84.92%). Oxidized copper amounts 14.57%.

The predominance of copper sulfides in the composition of the ore allows using of sulfhydryl collectors, namely sodium diisopropyldithio-phosphate at evaluating sorption and flotation in these systems.

Flotation and Adsorption. The results of the investigation of sodium diisopropyldithiophosphate adsorption and flotation of copper sulfide ore are shown in Figure 1.

Table 3 – Phase analysis of copper in the initial ore

Cu_{com}, %	Cu in the oxidized form			Cu in the sulfide form				$Cu_{water\text{-}soluble}$
	$Cu_{com.\ oxid.}$	$Cu_{bound.\ oxid.}$	$Cu_{free\ oxid.}$	$Cu_{com.\ sulph.}$	$Cu_{bound.}$ Chalcocite.	$Cu_{bound.}$ Bornite	$Cu_{\text{связ.}}$ Chalcopyrite	
1.99	0.28	0.26	0.02	1.69	1.16	0.52	0.01	0.02
100	14.07	13.07	1.01	84.92	58.29	26.13	0.50	1.01

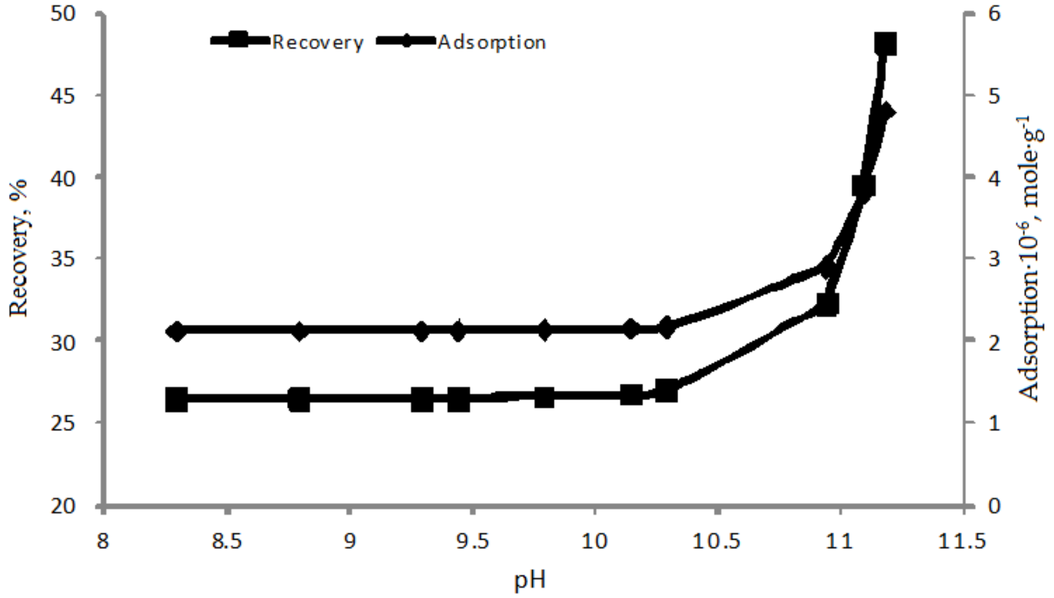

Figure 1 - The effect of pH on copper recovery and the adsorption of sodium diisopropyldithiophosphate ($C=4.25 \cdot 10^{-5}$ mole•L^{-1}) on copper sulfide ore

Analysis of the data shown in Figure 2 showed that the maximum copper recovery into the concentrate and the sorption of diisopropyldithiophosphate ions on the surface is observed at pH 11; this is due to oxidation-reduction processes involving sulfide minerals (chalcocite) and the replacement of sulfate ions by diisopropyldithiophosphate ions with the formation of less soluble compounds. The oxidation of sulfide ions occurs with low intensity at pH 8-10. Since in the ore the main copper-containing minerals are chalcocite and bornite, consideration of the equilibrium involving collectors will be carried out using the example of these minerals whose surface after immersion in aqueous solutions consists of three layers, the outer layer is represented by copper hydroxides, the middle layer - by elemental sulfur, the inner surface – by copper (I) sulfide. The outer layer dissolves at low and high pH of the medium; therefore, in the oxidation-reduction processes in the presence of oxygen, a layer of elemental sulfur participates. At low pH of medium 1-6, the oxidation-reduction pair S^{2-}/S predominates, at high pH 8-14, sulfur is oxidized to sulfate ions. Possible reactions (I-XIX) and equilibrium constants for the presented system are given in Table 4, where L is a diisopropyldithiophosphate ion $(i\text{-}C_3H_7O)_2PS_2^-$.

Table 4 - Oxidation-reduction reactions and equilibriums in systems Cu_2S-H_3O^+/OH^- – L^-, Cu_5FeS_4 - H_3O^+/OH^- – L^-

Reactions		The equilibrium constant / Standard potential, V
$Cu_2S_{(s)} = 2Cu^+ + S^{2-}$	(I)	$K_{sp1} = 10^{-48.12}$
$Cu_5FeS_4 = 5Cu^+ + Fe^{3+} + 4S^{2-}$	(II)*	$K_{sp2} = 10^{-134.29}$
$Cu^{2+} + e^- \rightarrow Cu^+$	(III)	$E^0_{Cu^{2+}/Cu^+} = 0.167$
$S^{2-} + 2e^- \rightarrow S^0$	(IV)	$E^0_{S^{2-}/S^0} = -0.48$
$2S^{2-} + 3H_2O + 8e^- \rightarrow S_2O_3^{2-} + 6H^+$	(V)	$E^0_{S^{2-}/S_2O_3^{2-}} = -0.547$
$S^{2-} + 8OH^- + 8e^- \rightarrow SO_4^{2-} + 4H_2O$	(VI)	$E^0_{S^{2-}/SO_4^{2-}} = -1.23$
$Cu^{2+} + OH^- = CuOH^+$	(VII)	$K_1 = 10^7$
$Cu^{2+} + 2OH^- = Cu(OH)_2$	(VIII)	$K_2 = 10^{13.68}$
$Cu^{2+} + 3OH^- = Cu(OH)_3^-$	(IX)	$K_3 = 10^{17}$
$Cu^{2+} + 4OH^- = Cu(OH)_4^{2-}$	(X)	$K_4 = 10^{18.5}$
$Fe^{2+} + OH^- = FeOH^+$	(XI)	$K_5 = 10^{5.5}$

Continuation of table 4

Reactions	The equilibrium constant / Standard potential, V
$Fe^{2+} + 2OH^- = Fe(OH)_2$ (XII)	$K_6 = 10^{7.4}$
$Fe^{2+} + 3OH^- = Fe(OH)_3^-$ (XIII)	$K_7 = 10^{11}$
$Fe^{2+} + 4OH^- = Fe(OH)_4^{2-}$ (XIV)	$K_8 = 10^{10}$
$Cu(OH)_{2(s)} = Cu^{2+} + 2OH^-$ (XV)	$K_{sp3} = 10^{-19.25}$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (XVI)	$E^0_{Fe^{3+}/Fe^{2+}} = 0.771$
$CuL_{2(s)} = Cu^{2+} + 2L^-$ (XVII)	$K_{sp4} = 10^{-19.42}$
$FeL_{2(s)} = Fe^{2+} + 2L^-$ (XVIII)	$K_{sp5} = 10^{-20.29}$
$L^- + H_3O^+ \leftrightarrow HL + H_2O$ (XIX)	$K_A = 10^{-5.59}$

* The value of K_{sp2} is calculated by the method of comparative calculation from dependence (reaction (II))

$$-\Delta_s\bar{G}^0_{298} = -1.0469 \cdot \left(-\Delta_f\bar{G}^0_{298}\right) + 118.85,$$

where:

$$-\Delta_s\bar{G}^0_{298} = (8.314 \cdot 2.303 \cdot 298 \cdot lnK_{sp2})/10$$

$$-\Delta_f\bar{G}^0_{298}(Cu_5FeS_4) = 32.2 \text{ kJ/mole·atom [16]}$$

The equation is derived from the data on the solubility product for the following minerals: $Cu_3(OH)_2(CO_3)_2$ (azurite), FeS_2 (pyrite), Cu_2S (chalcocite), $CuFeS_2$ (chalcopyrite), $Cu_2(OH)_2CO_3$ (malachite) and the average atomic energy of Gibbs. The correlation coefficient of the dependence is R = 0.99.

The mole fraction of the free anions of the precipitant (diisopropyldithiophosphate ions) [17]:

$$x_L = \frac{\frac{K_A^2}{[H_3O^+]^2}}{\left(1+\frac{K_A}{[H_3O]}\right)^2} = \frac{1}{\left(1+\frac{[H_3O^+]}{K_A}\right)^2} \qquad (1)$$

where K_A is the equilibrium constant of the reaction (XIX).

The mole fraction of the free metal ions:

$$x_{Kt} = \frac{1}{1+K_1[OH^-]+K_2[OH^-]^2+K_3[OH^-]^3+K_4[OH^-]^4} \qquad (2)$$

where K$_1$, K$_2$, K$_3$, K$_4$ are the stability constants of metal hydroxocomplexes (reactions (VII-X) for Cu(II) ions , (XI-XIV) for Fe(II)).

The real solubility constant of metal diisopropyldithiophosphates is:

$$K^{s,r}_{KtL_2} = \frac{K^s_{KtL_2}}{x_{Kt}x_L^2} \qquad (3)$$

where x_{Kt} is the mole fraction of the free metal ions, x_L is the mole fraction of the free anions of the precipitant (diisopropyldithiophosphate ions), $K^s_{KtL_2}$ is the solubility constant of metal (II) diisopropyldithiophosphate (reactions (XVII-XVIII)).

In acidic medium, copper sulfides are oxidized to elemental sulfur by reaction (IV), sulfide sulfur is oxidized to thiosulfate and sulfate ions in neutral (V) and alkaline (VI) mediums. Then the free concentration of metal ions not bound to a poorly soluble compound with a diisopropyldithiophosphate ion is:

$$x'_{Kt} = \frac{1}{1+(1/K^{s,r}_{KtL_2})[L^-]^2} \qquad (4)$$

where $K^{s,r}_{KtL_2}$ is the real solubility constant of metal diisopropyldithiophosphates, $[L^-]$ is concentration of diisopropyldithiophosphate-ions in solution.

The mole fraction of hydroxide-ions, not bounded with metal ions, is:

$$x_{OH^-} = \frac{1}{\left(1+\frac{10^{-pH}}{K_W}\right)^2} \qquad (5)$$

where K_W is the ionic product of water.

The real dissolution constant of copper (II) hydroxide is calculated by formula:

$$K^{s,r}_{Kt(OH)_2} = \frac{K^s_{Kt(OH)_2}}{x_{Kt}x^2_{OH^-}} \qquad (6)$$

where $K^s_{Kt(OH)_2}$ is the solubility constant of metal (II) hydroxide (reaction XV), x_{Kt} is the mole fraction of metal ions, not bounded to hydroxocomplexes, x_{OH^-} is the mole fraction of hydroxide-ions not bounded with metal ions.

The formation of the copper (II) hydroxide on the surface of the mineral is possible when chalcocine is dissolved in an alkaline solution. $Cu(OH)_2$ in the presence of diisopropyldithiophosphate ions forms a slightly soluble copper (II) diisopropyldithiophosphate as a result of the substitution reaction:

$$Cu(OH)_2 + 2L^- \overset{K_{exch}}{\longleftrightarrow} CuL_2 + 2OH^- \qquad \text{(XX)}$$

The exchange constant (K_{exch}) is calculated by formula:

$$K_{exch} = \frac{[OH^-]}{[L^-]} = \frac{K^{c,r}_{Cu(OH)_2}}{K^{c,r}_{CuL_2}} \qquad (7)$$

where $K^{c,r}_{Cu(OH)_2}$ is the real solubility constant of copper (II) hydroxide, $K^{c,r}_{CuL_2}$ is the real solubility constant of copper (II) diisopropyldithiophosphate.

From the data shown in Figure 2, it is evident that the most complete exchange process occurs at low pH of the medium from one to five pH units, in this medium, the mole fraction of copper (II) hydroxides is negligible, and copper (II) ions are bound to aqua-complexes.

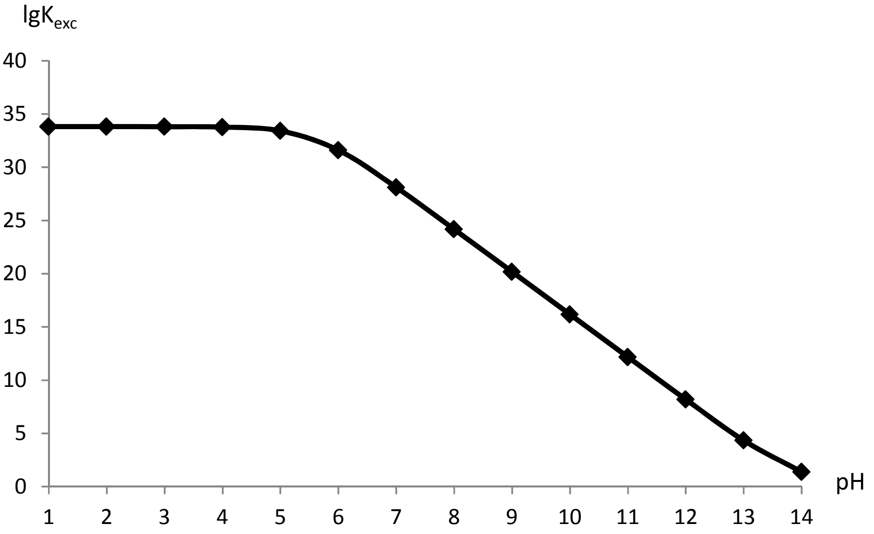

Figure 2 - The effect of pH on the exchange constant of hydroxide-ions on diisopropyldithiophosphate ions in the composition of a poorly soluble compound

However, as a result of red-ox processes involving copper (I) ions and sulfide ions, the formation of significant amounts of copper (II) ions and, consequently, diisopropyldithiophosphate complexes on the mineral surface is hampered by the formation of a film of elemental sulfur that reduces access of ligand ions to the mineral surface.

It was found that as the pH of the medium increases, the molar fraction of copper (II) hydroxides increases, this leads to a decrease in the exchange constant. However, the logarithm of the exchange constant at pH 14 is greater than zero, which indicates the predominance of the replacement of hydroxide ions by diisopropyldithiophosphate ions.

In connection with this, the real oxidation-reduction potential of the pair Cu^{2+}/Cu^+, was calculated, taking into account the influence of oxidation-reduction potentials of sulfide ions in acidic (8), neutral (9) and alkaline (10) mediums for chalcocite according to the equations:

$$Cu_2S \rightarrow 2Cu^{2+} + S^0 + 4e^- \qquad \text{(XXI)}$$

$$E^{\circ,r} = \overset{\circ}{E}_{S^{2-}/S^0} + \overset{\circ}{E}_{Cu^{2+}/Cu^+} + 0.059 \cdot z_{Cu^{2+}} \cdot lg\gamma_{Cu^{2+}} + 0.059 \cdot z_{Cu^{2+}} \cdot lgx'_{Cu^{2+}} \qquad (8)$$

where $z_{Cu^{2+}}$ is the amount of Cu (II) ions' moles, $\overset{\circ}{E}_{Cu^{2+}/Cu^{+}}$ is the standard potential of reaction III.

Chalcocite oxidizes in neutral medium by reaction:

$$2Cu_2S + 3H_2O \rightarrow 4Cu^{2+} + \\ + S_2O_3^{2-} + 6H^{+} - 12e^{-} \qquad \text{(XXII)}$$

$$E^{\circ,r} = \overset{\circ}{E}_{\frac{Cu^{2+}}{Cu^{+}}} + \left(\frac{0.059}{z}\right) \cdot \\ \cdot lg \frac{\gamma_{S_2O_3^{2-}} \cdot \gamma_{H_3O^{+}}^{z_{H_3O^{+}}}}{\gamma_{S^{2-}}^{2}} - \left(\frac{0.059 \cdot z_{H_3O^{+}}}{z}\right) \cdot \\ \cdot pH + \overset{\circ}{E}_{S^{2-}/S_2O_3^{2-}} + \\ + 0.059 \cdot z_{Cu^{2+}} \cdot lgx'_{Cu^{2+}} + \\ +0.059 \cdot z_{Cu^{2+}} \cdot lg\gamma_{Cu^{2+}} \qquad (9)$$

where $z_{Cu^{2+}}$ is the amount of Cu (II) ions' moles, $z_{H_3O^{+}}$ is the amount of hydroxonium ions' moles according to oxidation-reduction reaction, z is the number of electrons by reaction. Chalcocite oxidizes in alkaline medium according to the reaction:

$$Cu_2S + 8OH^{-} \rightarrow 2Cu^{2+} + \\ +SO_4^{2-} + 4H_2O - 10e^{-} \qquad \text{(XXIII)}$$

$$E^{\circ,r} = \overset{\circ}{E}_{\frac{Cu^{2+}}{Cu^{+}}} + \left(\frac{0.059}{z}\right) \cdot \\ \cdot lg \frac{\gamma_{SO_4^{2-}} \cdot \gamma_{OH^{-}}^{z}}{\gamma_{S^{2-}}} - \left(\frac{0.059 \cdot z_{OH^{-}}}{z}\right) \cdot \\ \cdot pH + \left(\frac{0.826 \cdot z_{OH^{-}}}{z}\right) + \\ +\overset{\circ}{E}_{S^{2-}/SO_4^{2-}} + + 0.059 \cdot z_{Cu^{2+}} \cdot \\ \cdot lgx'_{Cu^{2+}} + 0.059 \cdot z_{Cu^{2+}} \cdot lg\gamma_{Cu^{2+}} \qquad (10)$$

where $z_{Cu^{2+}}$ is the amount of Cu(II) ions' moles, $z_{OH^{-}}$ is the amount of hydroxide ions' moles according to oxidation-reduction reaction, z is the number of electrons according to the reaction.

Analogous calculations of the real oxidation-reduction potential of the Cu(II)/Cu(I) pair, taking into account the oxidation of sulfide and diisopropyldithiophosphate ions, the reduction of Fe(III) ions were carried out for bornite in acidic and weakly acidic mediums (11, 12) [18], neutral and alkaline mediums (13) [19]:

$$Cu_5FeS_4 + L^{-} \rightarrow 5Cu^{2+} + \\ +Fe^{2+} + \left(\frac{1}{2}\right) L_2 + 4S^0 + 13e^{-} \qquad \text{(XXIV)}$$

$$E^{\circ,r} = \overset{\circ}{E}_{\frac{S^{2-}}{S^0}} + \overset{\circ}{E}_{\frac{Cu^{2+}}{Cu^{+}}} - \overset{\circ}{E}_{\frac{Fe^{3+}}{Fe^{2+}}} + \overset{\circ}{E}_{\frac{L_2}{2L^{-}}} + \\ + \left(\frac{0.059}{z}\right) \cdot z_{Cu^{2+}} \cdot lg\gamma_{Cu^{2+}} + \\ + \left(\frac{0.059}{z}\right) \cdot z_{Cu^{2+}} \cdot lgx'_{Cu^{2+}} + \\ + \left(\frac{0.059}{z}\right) \cdot z_{Fe^{2+}} \cdot lg\gamma_{Fe^{2+}} + \\ + \left(\frac{0.059}{z}\right) \cdot z_{Fe^{2+}} \cdot lgx'_{Fe^{2+}} - \\ -z_{L^{-}} \cdot \left(\frac{0.059}{z}\right) \cdot lg\, x\square\, L\square — \\ -z_{L^{-}} \cdot \left(\frac{0.059}{z}\right) \cdot lg\gamma''_{L^{-}} \qquad (11)$$

where $\overset{\circ}{E}_{L_2/2L^{-}}$ is the oxidation-reduction potential of pair of diisopropyldithiophosphate-ion – disulfide equals to 0.196 B, $x_{L^{-}}$ is the mole fraction of not bounded ligands, $\gamma''_{L^{-}}$ is the activity coefficient of ligand in the solution, $z_{L^{-}}$ is the number of ligand moles, participating in the reaction, $\overset{\circ}{E}_{Fe^{3+}/Fe^{2+}}$ is the standard potential of reaction XVI.

In weakly acidic medium pH 2-5 bornite oxidizes according to the reaction:

$$Cu_5FeS_4 + L^{-} \rightarrow 2CuS + 2S^0 + \\ +3Cu^{2+} + Fe^{2+} + \left(\frac{1}{2}\right) L_2 + 9e^{-} \qquad \text{(XXV)}$$

$$\begin{aligned}
E^{\circ,r} = {} & E^{\circ}_{\frac{Cu^{2+}}{Cu^{+}}} - E^{\circ}_{\frac{Fe^{3+}}{Fe^{2+}}} + E^{\circ}_{\frac{L_2}{2L^{-}}} + \\
& + \left(\frac{0.059}{z}\right) \cdot lg \frac{\gamma^{3}_{Cu^{2+}} \cdot \gamma_{H_3O^+}^{z_{H_3O^+}}}{1} - \\
& - \left(\frac{0.059 \cdot z_{H_3O^+}}{z}\right) \cdot pH + E^{\circ}_{S^{2-}/_{S^0}} + \\
& + \left(\frac{0.059}{z}\right) \cdot z_{Cu^{2+}} \cdot lgx'_{Cu^{2+}} + \left(\frac{0.059}{z}\right) \cdot z_{Cu^{2+}} \cdot \\
& \cdot lg\gamma_{Cu^{2+}} + \left(\frac{0.059}{z}\right) \cdot z_{Fe^{2+}} \cdot lg\gamma_{Fe^{2+}} + \\
& + \left(\frac{0.059}{z}\right) \cdot z_{Fe^{2+}} \cdot lgx'_{Fe^{2+}} - z_{L^-} \cdot \left(\frac{0.059}{z}\right) \cdot \\
& \cdot lgx_{L^-} - z_{L^-} \cdot \left(\frac{0.059}{z}\right) \cdot lg\gamma''_{L^-}
\end{aligned} \tag{12}$$

For bornite, the process of surface oxidation under the action of dissolved oxygen in the pH range 5-14 proceeds according to the reaction:

$$\begin{aligned}
& (Cu_3FeS_4)^{2-} \cdot 2Cu^+ + 2H_2O + \\
& +L^- = 4S^0 + Fe^{2+} + Cu(OH)_2 + \\
& +2H^+ + \left(\frac{1}{2}\right) L_2 + 5e^-
\end{aligned} \tag{XXVI}$$

$$\begin{aligned}
E^{\circ,r} = {} & E^{\circ}_{\frac{Cu^{2+}}{Cu^{+}}} - E^{\circ}_{\frac{Fe^{3+}}{Fe^{2+}}} + E^{\circ}_{\frac{L_2}{2L^{-}}} + \left(\frac{0.059}{z}\right) \cdot \\
& \cdot lg \frac{\gamma_{H_3O^+}^{z_{H_3O^+}}}{1} - \left(\frac{0.059 \cdot z_{H_3O^+}}{z}\right) \cdot pH + E^{\circ}_{S^{2-}/_{S^0}} + \\
& + \left(\frac{0.059}{z}\right) \cdot z_{Fe^{2+}} \cdot lg\gamma_{Fe^{2+}} + \left(\frac{0.059}{z}\right) \cdot z_{Fe^{2+}} \cdot \\
& \cdot lgx'_{Fe^{2+}} - z_{L^-} \cdot \left(\frac{0.059}{z}\right) \cdot lgx_{L^-} - \\
& - z_{L^-} \cdot \left(\frac{0.059}{z}\right) \cdot lg\gamma''_{L^-}
\end{aligned} \tag{13}$$

The real potential of the oxidation-reduction process depends on the molar fraction of the potential-determining ions, copper (II) ions, which are not bound to a poorly soluble compound, calculated by formula (2) and the mole fraction of sulfide ions, which is calculated according to the formulas (14-16):

pH 1-6

$$x_{S^{2-}} = \frac{1}{1 + 10^{\frac{\left(E^{\circ,r} - E^{\circ}_{S^{2-}/S^0}\right) \cdot z}{0.059}}} \tag{14}$$

where $E^{\circ,r}$ is the real standard potential of pair Cu^{2+}/Cu^+, $E^{\circ}_{S^{2-}/S^0}$ is the real standard potential of pair S^{2-}/S^0, z is the number of electrons participating in the oxidation of sulfide sulphur.

pH 7

$$x_{S^{2-}} = \frac{1}{1 + 10^{\frac{\left(E^{\circ,r} - E^{\circ}_{S^{2-}/S_2O_3^{2-}}\right) \cdot z}{0.059}}} \tag{15}$$

where $E^{\circ}_{S^{2-}/S_2O_3^{2-}}$ is the real standard potential of pair $S^{2-}/S_2O_3^{2-}$.

pH 8-14

$$x_{S^{2-}} = \frac{1}{1 + 10^{\frac{\left(E^{\circ,r} - E^{\circ}_{S^{2-}/SO_4^{2-}}\right) \cdot z}{0.059}}} \tag{16}$$

where $E^{\circ}_{S^{2-}/SO_4^{2-}}$ is the real standard potential of pair S^{2-}/SO_4^{2-}.

For bornite the mole fraction of sulfide ions at pH 1-14 is calculated by formula:

$$x_{S^{2-}} = \frac{1}{1+10^{\frac{\left(E^{\circ,r} - E^{\circ}_{S^{2-}/S^0}\right) \cdot z}{0.059}}} \tag{17}$$

Since an insoluble compound is formed on the surface of the chalcocite, the real solubility constant which is calculated taking into account the influence of the pH of the medium, in formula (3), instead of the solubility constant of copper (II) diisopropyldithiophosphate, the solubility constant of chalcocite is used, and the mole fraction of the anion is replaced by the mole fraction of the sulfide ion, manifesting as a precipitator.

The real solubility constant of copper (I) sulfide:

$$K^{s,r}_{Cu_2S} = \frac{K^{s}_{Cu_2S}}{x^2_{Cu^+} x_{S^{2-}}} \qquad (18)$$

where $K^{s}_{Cu_2S}$ is the solubility product of copper sulfide (I) (reaction I), $x_{S^{2-}}$ is the mole fraction of sulfide ions (14-16), x_{Cu^+} is the mole fraction of copper (I) ions, determining by equation:

$$x_{Cu^+} = \frac{1}{1+10^{\frac{\left(E^{\circ,r}-E^{\circ}_{Cu^{2+}/Cu^{+}}\right)\cdot z}{0.059}}} \qquad (19)$$

where z is the number of electrons participating in the reaction I.

$pK^{s,r}$ is calculated by equation:

$$pK^{s,r} = -logK^{s,r}_{Cu_2S} \qquad (20)$$

The real solubility constant of bornite:

$$K^{s,r}_{Cu_5FeS_4} = \frac{K^{s}_{Cu_5FeS_4}}{x^5_{Cu^+} x_{Fe^{3+}} x^4_{S^{2-}}} \qquad (21)$$

where $K^{s,r}_{Cu_5FeS_4}$ is the solubility product of bornite (reaction II), $x_{S^{2-}}$is the mole fraction of sulfide ions (17), x_{Cu^+} is the mole fraction of copper (I) ions (19).

$x_{Fe^{3+}}$ is the mole fraction of iron (III) and calculated by equation:

$$x_{Fe^{3+}} = \frac{1}{1+10^{\frac{\left(E^{\circ}_{Fe^{3+}/Fe^{2+}}-E^{\circ,r}\right)\cdot z}{0.059}}} \qquad (22)$$

where z is the number of electrons participating in the reaction XVI.

$pK^{s,r}$ is calculated by equation:

$$pK^{s,r} = -logK^{s,r}_{Cu_5FeS_4} \qquad (23)$$

The results of calculating the changes in the real solubility constant ($pK^{s,r}$) of chalcocite and bornite in the presence of a flotation agent - sodium diisopropyldithiophosphate from the pH of the medium are shown in Figures 3-4.

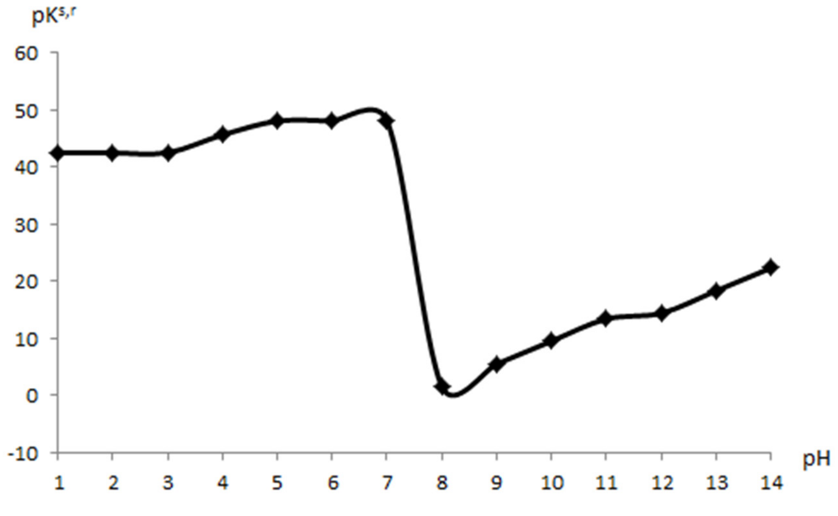

Figure 3 – Dependence of the real solubility constant ($pK^{s,r}$) of chalcocite in the presence of a flotation agent ($C=4.25\cdot10^{-5}$ mole$\cdot$L^{-1}) on the pH of the mineral suspension

Analysis of the real solubility constant ($pK^{s,r}$) showed that the stability of chalcocite in the presence of sodium diisopropyldithiophosphate with increasing pH of the solution in acidic media remains constant up to pH 3, in the pH range 4-7, chalcocite stability increases. The maximum solubility constant for chalcocite is observed at pH 7, which is associated with oxidation to thiosulfate ions in the presence of oxygen, since copper (II) thiosulfate is less soluble. In the transition to a slightly alkaline medium pH 8, the real solubility constant decreases sharply, this process corresponds to the formation of sulfate ions and copper (II) ions on the chalcocite surface, followed by the replacement of diisopropyldithiophosphate ion and the formation of copper (II) ion complexes that are physically adsorbed. At pH 8-14, there is an increase in solubility of chalcocite $pK^{s,r}$, associated with the formation of sparingly soluble copper (II) diisopropyldithiophosphates.

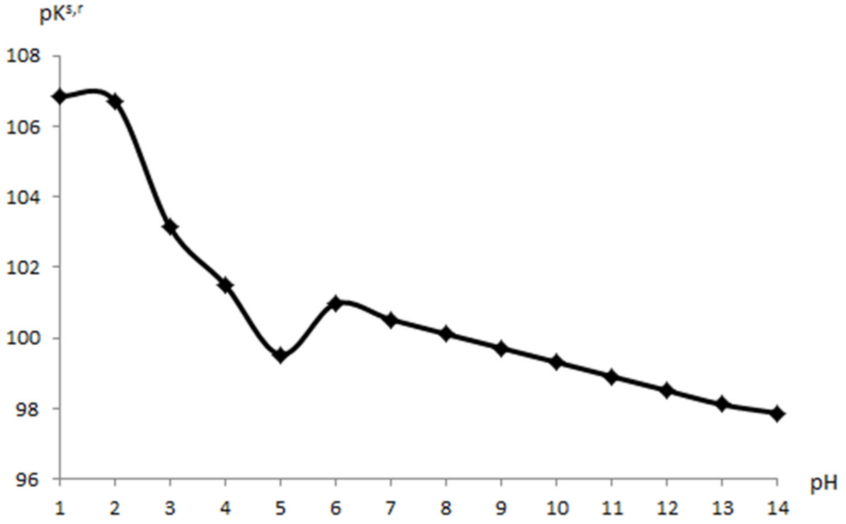

Figure 4 – Dependence of the real solubility constant ($pK^{s,r}$) of bornite in the presence of a flotation agent ($C=4.25\cdot10^{-5}$ mole•L^{-1}) on the pH of the mineral suspension

It is shown that in an acid medium pH 1-2 bornite has minimal solubility due to the presence of elemental sulfur on the surface. Increasing pH of the solution to 5 leads to an increase in solubility due to the formation of iron (III) hydroxide, which forms iron (III) diisopropyldithiophosphate, then this compound disproportionates to iron (II) diisopropyldithiophosphate and disulfide. Covellite is also formed on the surface of bornite particles at pH 5.

It is shown that in the pH range 6-14, the iron (III) diisopropyldithiophosphate formed enters oxidation-reduction reactions, the product of which is the disulfide, which is fixed on the surface by means of van-der-Waals bonds, this causes the sorption of the collector.

Therefore, flotation of chalcocite and bornite in acidic and neutral mediums is impossible, flotation ability of chalcocite and bornite increases in the pH range 8-12. This also indicates the dependence of the reactivity of the mineral on the pH of the solution. Further, infrared spectra of flotation agents on the surface of the ore were removed.

FT-IR spectroscopy. To explain the mechanism of adsorption of the flotation agent on the surface of the ore, the IR spectra of the flotation agent, ore and ore after the sorption of the flotation agent were considered (Figure 5).

The IR spectrum of sodium diisopropyldithiophosphate there are absorption bands in the region of 2888-2963 cm^{-1}, which corresponds to stretching vibrations of CH-bonds. The dithiophosphate radical is characterized by absorption bands at 520-560 cm^{-1} and 630-680 cm^{-1}, related to the ν(P-S) and ν(P=S) coordinated PS_2-groups, respectively. IR-Fourier spectrum (cm^{-1}): 1458, 1430, 1307 (νCH2); 1085, 1034, 990 pl., 966 (νC-O); 778, 736 pl. (νP-O), 2370 cm^{-1} (νS-H). The absorption bands at 989 and 969 cm^{-1} are characteristic for the P-O-R fragment oscillation. The figure also shows the IR-Fourier-spectrum of sulfide copper ore. The spectrum contains a broad absorption band in the region of 3000-3500 cm^{-1}, which corresponds to OH-groups, absorption bands at 1105, 983 cm^{-1} are characteristic for SO_4^{2-} groups, 879 cm^{-1} for CO_3^{2-} groups, 1080 cm^{-1} for PO_4^{3-} groups. Analysis of the IR Fourier spectrum of the ore treated with a flotation agent solution showed that there is an absorption band at 1000 cm^{-1} that is characteristic of the P-O-R fragment oscillation. In the region of 2800-3000 cm^{-1}, new absorption bands appear which characterizes the trace amounts of a flotation reagent of an organic nature. Perhaps this flotation agent has not entered into a chemical interaction with the mineral, but only physically adsorbed on the surface of its particles. After contact of the ore with 1·10^{-5} M solution of dithiophosphate in a weakly alkaline medium, the maxima of the characteristic frequencies of the P=S (680,669 cm^{-1}) and PS (590, 560, 525.5 cm^{-1}), toward low frequencies by 10 cm^{-1} for P=S bond and by 2-5 cm^{-1} for PS bond, on the basis of which it is possible to assume the formation of bidentate-cyclic coordination of ligands with a metal via both sulfur atoms. The formation of additional bands with maxima in the frequency range of 610 and 575 cm^{-1} indicates, possibly, the formation of bonds of ore components with sulfur atoms of the reagent. The position of these bands is shifted in comparison with the position of similar bands in the IR spectrum of the flotation agent this indicates the coordination of $(i\text{-}C_5H_{11}O)_2PS_2^-$-ions on the ore surface. The position of the bands ν(PS_2) is shifted by 3-4 cm^{-1} to the low frequency region, and the position of the bands ν(P-O-R) has shifted by 6 cm^{-1} and 31 cm^{-1} to the high-frequency region.

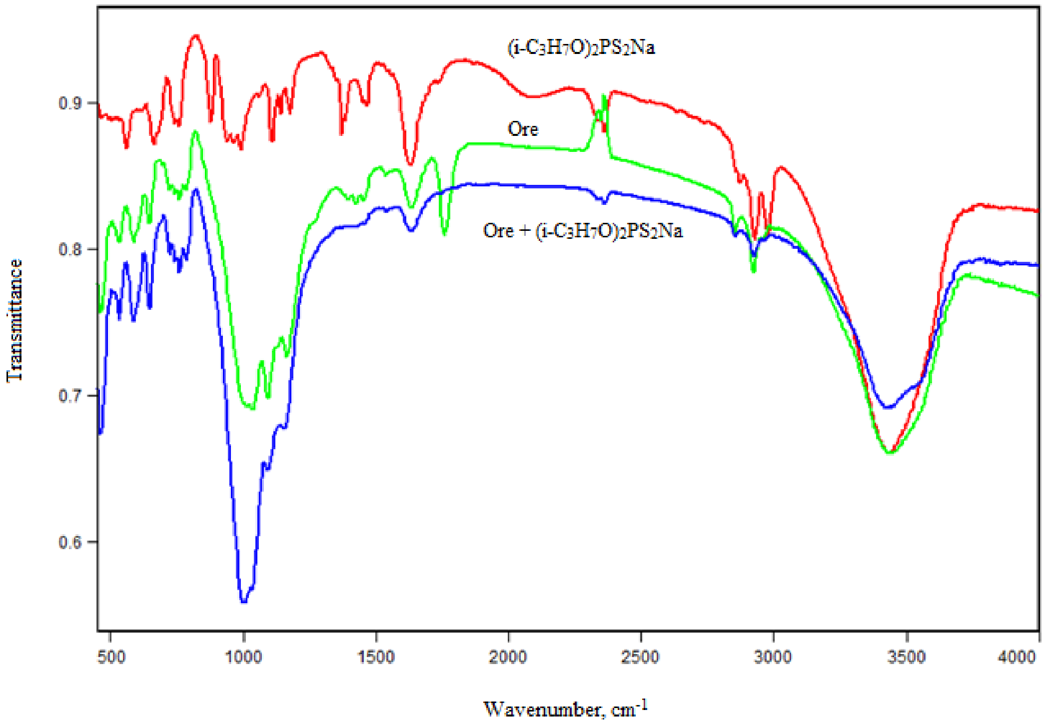

Figure 5 – FT-IR spectra of collector, sulfide copper ore and sulfide copper ore treated with collector after treatment

Conclusion

Elemental analysis of samples of copper sulfide ore was carried out, copper content in ore equals to 1.99%. According to the results of the mineralogical analysis, copper-containing sulfide minerals contain chalcocite, bornite. It is shown that the sorption capacity increases with increasing pH of the medium from 10.5-11.5. It has been established that oxidation-reduction processes play the main role in fixing the collector of diisopropyldithiophosphate ion. In a weakly alkaline medium, the sorption of the collector does not change with increasing pH, which is due to the formation of copper (II) complexes, as well as the disulfide fixed through Van-der-Waals bonds. While in the alkaline medium the collector anion forms strong coordination bonds with the metal ions of the crystal lattice of the mineral. Correlation of extraction of copper in concentrate during flotation enrichment with the value of sorption is revealed, which indicates a high sorption capacity of the collector at pH 10.5-11.5. FT-IR-spectroscopic analysis of ore samples was conducted, according to which it was established that the collector is coordinated with the ions of the metal of the crystal lattice of copper-containing minerals through the sulfur atoms of the dithiophosphate group.

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