

Fundamentals Of Xanthenes And Dixanthenes Interaction With Galena

M. Chettibi, A.A. Abramov, A. Boutrid

ABSTRACT: The results of thermodynamic analysis of flotation systems, chemical computation and experimental researches with the use of radiochemistry, electrochemistry, spectroscopy and flotation provided fundamental information on the conditions and possibility of xanthate and dixanthogen interaction with the freshly exposed and oxidizing galena surface, the composition of the adsorption layer of collector on the mineral surface depending on pH and redox-potential values, the optimal values of pH and redox-potential of pulp for efficient flotation of galena.

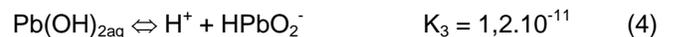
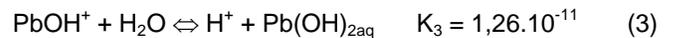
Key words: Galena surface, xanthenes, dexanthenes, flotation, modeling, thermodynamic analysis, surface stability.

INTRODUCTION

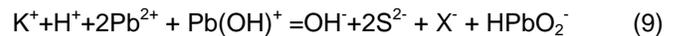
Galena PbS – the main lead sulphide mineral in ores-is the main object of numerous investigations of sulphidric collector interaction with sulphide minerals (A. A. Abramov, 1978, 1983) Contradiction in results and conclusions of researches carried out is conditioned by either not taking into account the state of galena surface, its oxidation degree or the influence of pH and redox-potential of pulp on the ratio of collector forms sorption and this ratio on floatability of mineral as well as erroneous conceptions on improvement of minerals floatability with increase in the sorption density of collector on its surface etc. The purpose of the paper is determination on the base of results of theoretical and experimental investigation the regularities of xanthate and dixanthogen interaction with the galena surface and the influence of their forms sorption on floatability of the mineral.

1. CONDITIONS FOR INTERACTION OF XANTHATE IONS WITH THE NON-OXIDIZED SURFACE OF GALENA

For evaluation of the possibility for interaction of xanthate ions X⁻ with the non-oxidized sulphide surface of galena it is necessary to use the system of equations from the expressions for equilibrium Constant of reaction of dissociation and hydrolysis for various ionic components being in solution:



Ionic product of water ($K_w = 1.10^{-14}$), equation of electro-neutrality of system:



and balance equation:

$$[\text{K}^+] = [\text{X}^-] + [\text{HX}] \quad (10)$$

Computation of the equations system received allows finding the relationship between the xanthate ions concentration [X⁻] securing formation of lead xanthate on the non-oxidized sulphide surface of galena and the pH value of solution:

$$[\text{X}^-]^4 = \frac{\{K_5 K_6 K_7^2 (K_2 [\text{H}^+]^3 + K_w [\text{H}^+]^2 + K_3 K_w [\text{H}^+] + K_3 K_4 K_w)\}}{\{K_1 K_2 [\text{H}^+]^3 (K_5 K_6 + K_6 [\text{H}^+] + [\text{H}^+]^2)\}} \quad (11)$$

results of computation by the equation (11) show that the non-oxidized sulphide surface of galena can interact with X⁻ forming lead xanthate. However, for that it is necessary to create rather a high concentration of X⁻ ions in solution. For example, for ethyl xanthate it makes (in mol/l): 2,7.10⁻³ (pH 3); 9,8.10⁻² (pH 8); 3,2.10⁻² (pH 9); 0,1 (pH 10); 0,25 (pH 11); 1,86 (pH 12). Results received confirm conclusions of many researches and, in particularly, explain the absence of formation of lead xanthate on the non-oxidized galena surface at the concentration of ethyl xanthate 3.10⁻⁴ mol/l in distilled water (Bogdanov et.al., 1980; Poling., Leja, 1963).

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2. EVALUATION OF THE POSSIBILITY OF XANTHATE IONS OXIDATION TO DIXANTHOGEN MOLECULES ON THE NON-OXIDIZED GALENA SURFACE

The possibility of xanthate ions X^- oxidation till dixanthogen molecules X_2 on the oxidized galena surface will be determined by its potential value. To evaluate the quantitative relationship between concentrations of X^- and X_2 it is possible to make use of reactions:



expressed through equations of reactions of the hydrogen electrode:

$$E_{PbS} = -0,980 - 0,0295 \cdot \lg [S^{2-}] \quad (14)$$

$$E_X = +0,029 - 0,0295 \cdot \lg [EtX^-] + 0,059 \cdot \lg [EtX] \quad (15)$$

On the base of equations (14) and (15) at $E_{PbS} = E_X$

$$\lg \left(\frac{[EtX_2][S^{2-}]}{[X^-]^2} \right) = -34,2;$$

From where

$$[EtX_2] = 6,3 \cdot 10^{-35} \left(\frac{[X^-]^2}{[S^{2-}]} \right) \quad (16)$$

If $[X^-]$ answers the $[X^-]$ necessary for formation of lead xanthate on the non-oxidized sulphide surface of galena, on the basis of expressions for equilibrium constants of reaction (1) and (7):

$$[X^-]^2 / [S^{2-}] = K_7 / K_1 = 2,43 \cdot 10^{+11} \text{ and}$$

$$[X_2] = 6,3 \cdot 10^{-35} \cdot 2,43 \cdot 10^{+11} = 1,5 \cdot 10^{-23} \text{ mol/l.}$$

The $[X_2]$ value received by 20-22 orders is less than $[X^-]$. Therefore, X^- ions cannot oxidize on the sulphide surface of galena and X_2 molecules should practically completely reduce till X^- . The latter must be taken into account in consideration of the collector mechanism action in processes carried out with the use of sodium sulphide or hydrosulphide.

3- EVALUATION OF THE POSSIBILITY OF DIXANTHOGEN INTERACTION WITH THE NON-OXIDIZED GALENA SURFACE

Interaction of dixanthogen with the Sulphide surface of galena can be represented on the base of reactions (1), (7), (13) and (17)



by the following way:



For EtX ΔF^0 of the reaction (18) is equal 4,9 ccal, the value of

$$K = 1/[EtX_2] = 3,9 \cdot 10^{+3} \text{ and, therefore, } [EtX_2] = 2,57 \cdot 10^{-4} \text{ mol/l.}$$

Thus, ethyl dixanthogen can directly interact with the non-oxidized sulphide surface of galena with formation of lead xanthate and elemental sulphur. Its concentration necessary for it makes up $2,57 \cdot 10^{-4}$ mol/l at all pH values. One should take into account, however, that solubility of ethyl dixanthogen in water is less and makes only about $1 \cdot 10^{-5}$ mol/l. Exceeding of this of this concentration results in yield of the X_2 excess in the form of the separate phase. As the activity of matter in the separate phase (being in the water solution) is close to the unit it is possible to say about the possibility of the interphase interaction of dixanthogen and the sulphide surface of galena (with formation of lead xanthate) already at the dixanthogen concentration only insignificantly exceeding its solubility. Formation of lead xanthate, obviously, will be accompanied by its dissolution till the concentration of xanthate ions in solution may occur also at the expense of X_2 by its reduction till X^- on the galena surface. Reduction of X_2 till X^- side by side with formation of lead xanthate on the galena surface is testified by results of researches carried out in "oxygen free" condition (Poling and Leja, 1963) and in the presence of excess of sulphide ions in solution (Abramov, 1978). It is possible to suppose that the process of X_2 reduction till X^- ions is not momentary and at the sufficient charges of X_2 non-reduced yet X_2 can co-adsorb on the underlining of chemisorbed collector. It will lead to formation of the "mixed" collector layer on the surface and flotation of the mineral (Abramov, 1978) though $[X^-]$ in solution being less of the necessary one for lead xanthate formation (see unit 2).

4- CONDITIONS FOR XANTHATE IONS INTERACTION WITH THE OXIDIZING GALENA SURFACE

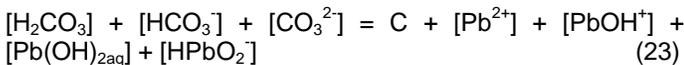
It is necessary to take into consideration in evaluation of the possibility of xanthate ions interaction with the oxidizing surface of galena that usual conditions (at the temperature $25^\circ C$) the concentration of oxygen dissolved in water makes $1,2 \cdot 10^{-3}$ mol/l and the summary concentration of carbon-bearing components – 10^{-5} mol/l (Garrels and Christ, 1965; Abramov, 1983), final oxidation products of galena being $PbCO_3$ (at pH from 7 till 9,0 – 9,5) or $Pb_3(CO_3)_2$ (at pH 9,0-9,5 till 12) (Abramov, 1978, Abramov and Avdokhin, 1997). Because of decreasing of sulphide ions concentration in oxidation conditions and aspiration of the system to preservation of the solubility product of galena the concentration of Pb^{2+} ions in solution will be increasing until its value will turn sufficient for formation of corresponding oxide lead compounds (at the available concentration of CO_3^{2-} and OH^- ions). After this the concentration of Pb^{2+} ions will be controlled by the solubility product of forming lead carbonate or hydro carbonate. Therefore, proceeding from conditions of equilibrium: Product of oxidation \rightleftharpoons lead xanthate, it is possible to determine the necessary X^- ions concentration securing formation of lead xanthate in the interaction of X^- as directly with the sulphide surface of oxidizing galena and with the already available oxidation product on its surface. For the equilibrium $PbCO_3$ (pH from 7 till 9,0 – 9,5) the minimum – necessary concentration X^- can be computed by the equation:

$$K_2 K_9 [H^+]^3 ([H^+]^2 + K_{11} [H^+] + K_{10} K_{11}) [X^-]^4 - CK_2 K_7 K_{10} K_{11} [H^+]^3 [X^-]^2 - K_7^2 K_{10} K_{11} (K_2 [H^+]^3 + K_w [H^+]^2 + K_w K_3 [H^+] + K_3 K_4 K_w) = 0 \quad (19)$$

Obtained by computation of the system of equations made up from expressions for equilibrium constants of reactions (2) – (4), (7), reactions:



and the balance equation:



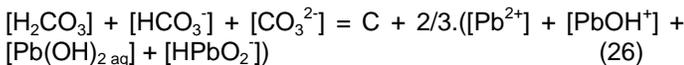
While the concentration of X^- corresponding to equilibrium $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 \rightleftharpoons \text{PbX}_2$ (pH from 9,0 – 9,5 till 12) – by equation:

$$\begin{aligned} & 9K_2^2 K_{12} [\text{H}^+]^8 ([\text{H}^+]^2 + K_{11} [\text{H}^+] + K_{10} K_{11})^2 [X^-]^{10} - \\ & 9C^2 K_2^2 K_7^3 K_{10}^2 K_{11}^2 K_w^2 [\text{H}^+]^6 [X^-]^4 - \\ & 12CK_2 K_7^4 K_{10}^2 K_{11}^2 K_w^2 [\text{H}^+]^3 (K_2 [\text{H}^+]^3 + K_w [\text{H}^+]^2 + K_3 K_w [\text{H}^+] + \\ & K_3 K_4 K_w) [X^-]^2 - \\ & - 4K_7^5 K_{10}^2 K_{11}^2 K_w^2 (K_2 [\text{H}^+]^3 + K_w [\text{H}^+]^2 + K_3 K_w [\text{H}^+] + K_3 K_4 K_w)^2 = 0 \quad (24) \end{aligned}$$

also received by computation of the system of equations made up from expressions for equilibrium constants of reaction (2) – (4), (7), (21), (22), reaction:



and the balance equation:



The concentration of ethyl xanthate computed by equations (19) and (24) are close to their values observed in practice of galena flotation and make up (mol/l):

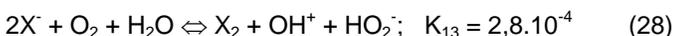
1,4.10⁻⁶ – at pH 7; 4,5.10⁻⁶ – at pH 8; 1,4.10⁻⁵ – at pH 9; 9,5.10⁻⁵ – at pH 10; 3,2.10⁻⁴ – at pH 11; 1,5.10⁻³ – at pH 12.

5- EVALUATION OF THE POSSIBILITY FOR X^- IONS OXIDATION TO X_2 MOLECULES AND REDUCTION OF X_2 MOLECULES TO X^- IONS ON THE SURFACE OF OXIDIZING GALENA

On the basis of the reaction (13) and the reaction:



Oxidation of X^- till X_2 and reduction of X_2 till X^- are proceeding by reaction:



as by the reaction (28) $[\text{HO}_2^-] = [\text{OH}^-]$, then

$$K_{13} = ([X_2][\text{OH}^-]^2)/([X^-]^2[\text{O}_2]),$$

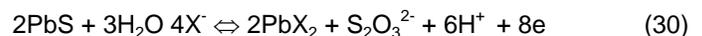
from where

$$[X_2] = K_{13} [\text{O}_2][X^-]^2 / [\text{OH}^-]^2 \quad (29)$$

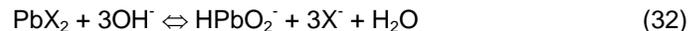
that is the X_2 concentration is determined by the ratio of X^- , O_2 , OH^- concentration in the solution. At the concentration of oxygen dissolved in water 1,2.10⁻³ mol/l and values of $[X^-]$ computed by equations (19) and (24) the equilibrium concentration of ethyl dixanthogen will make up (mol/l): 6,6.10⁻⁵ at pH 7; 6,8.10⁻⁶ at pH 8; 6,6.10⁻⁷ at pH 9; 3,0.10⁻⁷ at pH 10; 3,6.10⁻⁸ at pH 11; 7,6.10⁻⁸ at pH 12. Thus, ethyl X^- can be oxidized to X_2 whilst X_2 can be reduced to X^- in conditions of galena oxidation.

6- DIAGRAM OF THERMODYNAMIC STABILITY OF THE GALENA-XANTHATE –WATER SYSTEM

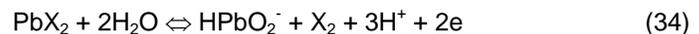
To compute the diagram of thermodynamic stability of the system: galena-xanthate-water (in potential E-pH coordinates) is possible using reactions and equations:



$$E = +0,170 - (3/4).0,059\text{pH} - (1/2).0,059\lg[X^-] + (1/8).0,059\lg[\text{S}_2\text{O}_3^{2-}] \quad (31)$$



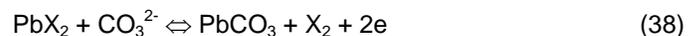
$$\lg[\text{HPbO}_2^-] + 3\lg[X^-] - 3\lg[\text{OH}^-] = -2,2 \quad (33)$$



$$E = +1,428 - (3/2).0,059\text{pH} + (1/2).0,059\lg[\text{HPbO}_2^-] + (1/2).0,059\lg[X_2] \quad (35)$$



$$E = +0,413 - (1/3).0,059\text{pH} - (1/3).0,059\lg[\text{CO}_3^{2-}] - (1/2).0,059\lg[X_2] \quad (37)$$



$$E = +0,238 - (1/2).0,059\lg[\text{CO}_3^{2-}] + (1/2).0,059\lg[X_2] \quad (39)$$

Results of computation by equations (31), (33), (35), (37), (39) are shown in fig.1.

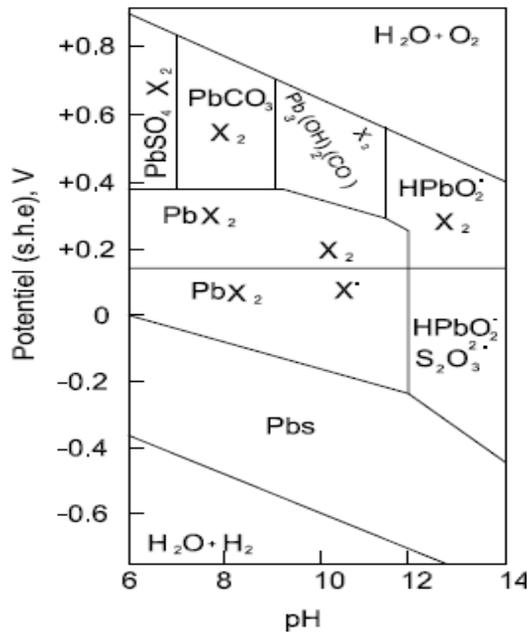


Figure 1. Diagram of the thermodynamic stability of the system: galena – xanthate – water at the concentration of butyl xanthate 10^{-4} mol/l.

7- RESULTS OF EXPERIMENTAL INVESTIGATIONS AND THEIR DISCUSSION

The reliability of the computed diagram: potential – pH (Fig.1) is proved by results of electrochemical investigations. For example, in Fig. 2 the comparing of anode potentiodynamic polarization curves of galena in the phone solution of 0,5 N.Na₂SO₄ (curve 1) and in the solution of sodium butyl xanthate (curve 2) is shown. In the presence of xanthate the anode potentiodynamic polarization curve (Fig.2, curve 2) is moved as compared with the phone one (Fig. 2, curve 1) to the side of more positive potentials and consistently two maximum of current: at the potential values $-0,100$ V and $+0,094$ V are observed on it.

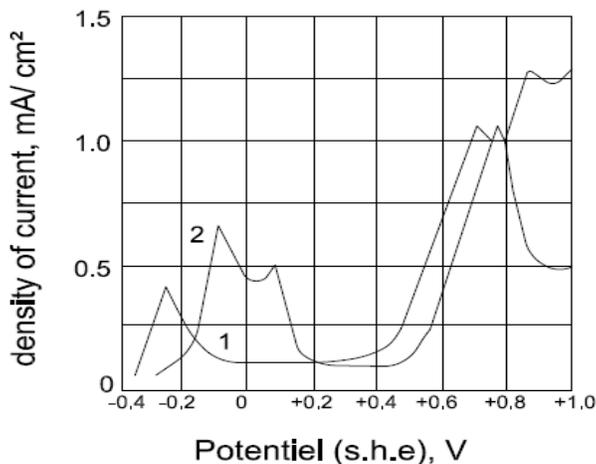


Figure 2. Anode potentiodynamic curves of the galena electrode in the solution of 0,5 N Na₂SO₄ without collector (1) and in the presence of $2,2 \cdot 10^{-4}$ mol/l butyl xanthate (2) at pH 9,5 and the spreading out speed of the potential 50 mV/min.

In conformity with the results of computation of the thermodynamic stability of the system (Fig.1) the first anode maximum can be explained by formation on the galena surface of lead xanthate by the reaction (30) which potential in investigated conditions is equal $-0,120$ V, whilst the second maximum – by formation of dixanthogen in the near – electrode layer by reaction (13). Increase in the current value in this case is connected with proceeding of xanthate oxidation side by side with oxidation of the galena surface. In its turn, the increase in the current value in the region of the transpassive state of galena is possible to explain by destruction of the collector adsorption coverage at the high positive values of the potential due to the desorption of dixanthogen molecules and tearing off of chemical interaction xanthate – galena products from the surface in such oxidizing conditions. Oxidation of X⁻ till X₂ by dissolved oxygen should be considered as the surface reaction so fast as in the absence of a mineral phase even at the prolonged aeration of xanthate solution the marked decrease in the X⁻ concentration did not observe (Abramov, 1978). Results of investigations with the use of methods radiochemistry, electrochemistry, froth less flotation (Melik – Gaikazian at al., 1990) and special method for quantitative determination of forms of collector sorption (Abramov, 1978) testify the X₂ formation in the sorption layer of xanthate on the galena surface (Fig. 3, a). The maximum share of it $(1 - \theta)$ in the sorption layer is observed in the neutral medium decreasing with increasing in the pH value of solution. Side by side with X₂ formation the part of xanthate is fixed by chemically (curve Γ). It is proved as displacement of the electrode potential value of galena to the negative side (curve $\Delta\phi$) and correlation of Γ and $\Delta\phi$ curves (Fig. 3, a). The existence of the determined ratio between concentrations of X⁻ and X₂ in solution in the presence of the mineral phase is conformed by that the treatment of galena with the oxidized surface by the X₂ solution lead, on principle, to the same results (Fig.3, b) as the treatment of the mineral by the X⁻ solution (Fig.3, a). In both cases, as it follows from the given above results of thermodynamic computation, the mixed coverage of collector consisting of the chemically fixed xanthate and physically sorbed dixanthogen is formed on the galena surface (Fig. 3, a, b). The presence of dixanthogen in the sorption coverage exerts the essential influence on the galena floatability. For example, at the same sorption density of xanthate equal 0,65 % of the conditional monolayer galena is floated completely, if about 20 % the sorbed collector is represented by dixanthogen (Fig. 3, curves $\Gamma_0, \gamma_0, \theta$ at pH 11), and only by 10 – 13 %, if there is no dixanthogen in the sorption coverage (Fig. 3, curves Γ, γ , at pH 10).

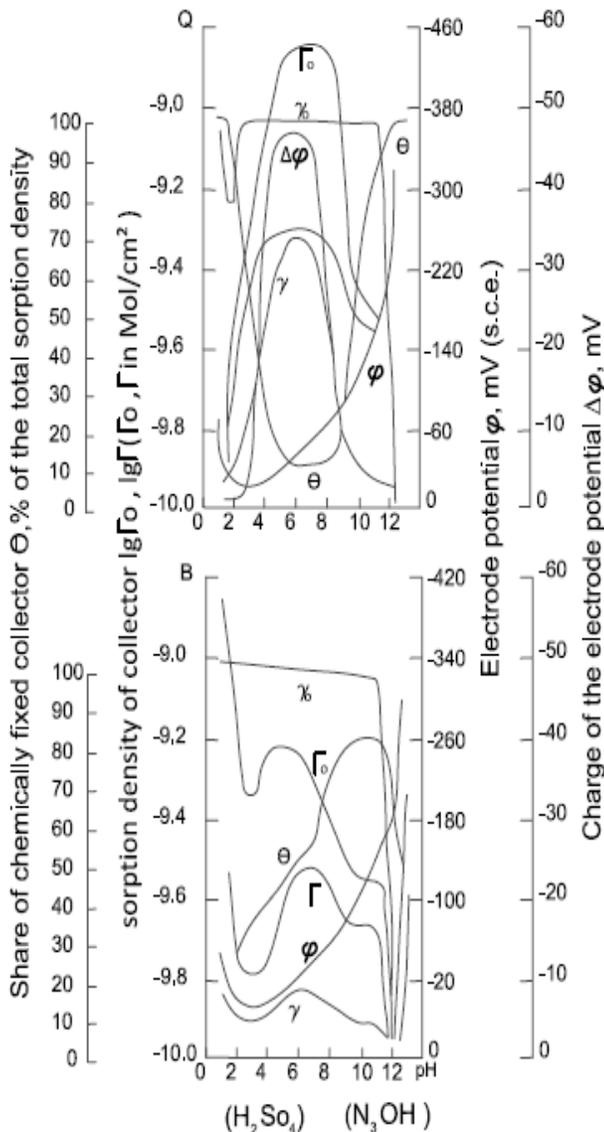


Figure 3. Influence of pH on the electrode potential value of galena in the absence of collector (φ), its change ($\Delta\varphi$) at the constant initial concentration of collector as well as on the sorption density (Γ_0 , Γ) of butyl xanthate (a) and butyl dixanthogen (b) and floatability of galena (γ_0 , γ) before (Γ_0 , γ_0) and after (Γ , γ) removal of physically absorbed dixanthogen molecules from its surface. (The initial concentration of collector in tests –10 mg/l).

The same results have been received with other sulphides (Abramov, 1978). In all cases the most efficient flotation of sulphide minerals is secured at the simultaneous presence in the adsorption layer on the mineral surface both chemically fixed xanthate and physically sorbed dixanthogen molecules (Fig. 4).

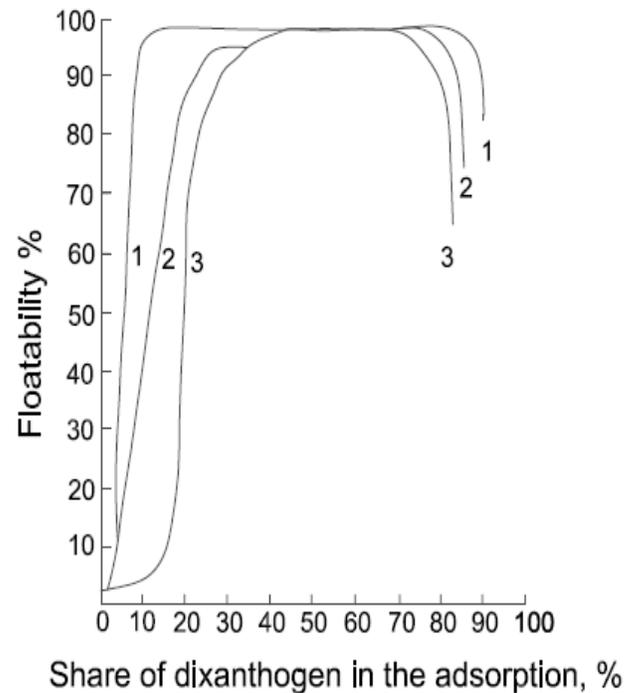


Figure 4. Influence of the contents of physically sorbed dixanthogen in adsorption coverage on floatability of galena (1), chalcopyrite (2) and pyrite (3) at the constant total sorption density of butyl xanthate (45 – 55 % of conditional monolayer) on their surface.

CONCLUSION

As a results of thermodynamic analyses of flotation systems, chemical computations and experimental researches with the use of radiochemistry, electrochemistry, spectroscopy and flotation it has been established: Conditions for xanthate interaction with the fresh exposed galena surface and impossibility of dixanthogen formation on it; The necessary xanthate concentration values in solution for formation of xanthate – bearing compounds on the galena surface in usual conditions and conditions of xanthate ions oxidation till dixanthogen interaction with the surface of oxidizing galena; The composition of xanthate and dixanthogen interaction with the galena surface depending on values of pH and oxidation – reduction potential of pulp; The ratio of chemical and physical form of xanthate or dixanthogen sorption on the galena surface necessary for its flotation and depression; The optimal values of pH and oxidation – reduction potential of pulp for efficient flotation of galena.

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