



ISSN: 0975-833X

## RESEARCH ARTICLE

### OPTIMAL CONDITIONS OF GALENA FLOTATION

\*<sup>1</sup>Chettibi, M., and <sup>2</sup>Abramov, A. A.

<sup>1</sup>Annaba University, BP12- Algeria, Faculty of Earth Sciences, Mining Department, Annaba 23000, Algeria

<sup>2</sup>Moscow State Mining University, Leninskii pr. 6, 117049 Moscow, Russia

#### ARTICLE INFO

##### Article History:

Received 24<sup>th</sup> July, 2013

Received in revised form

08<sup>th</sup> August, 2013

Accepted 10<sup>th</sup> September, 2013

Published online 23<sup>rd</sup> October, 2013

##### Key words:

Flotation,

Galena,

Thermodynamic analysis,

Modeling,

Environment.

#### ABSTRACT

Main idea to prevent the ground contamination by heavy metals is to extract them maximally with minimum consumption of chemical reagents. So, a perfect studying of pulp ionic structure, an adjustment of the sulphuric ores flotation parameters and modelling of minerals selectivity variables, by using thermodynamic method of analysis, the behaviour of lead xanthenes surface state in solution and experimental investigations results, allow obtaining quantitative physico-chemical models of minimum necessary xanthenes concentration of lead sulphide complete flotation. The optimal pH values ensuring a complete flotation of galena are agree with the potential of zero or minimum charge of its surface, and the optimal composition of the collector sorption layer consisting both of chemisorbed xanthenes and physically adsorbed dixanthenes. In additional, it was obtained quantitative models for the necessary xanthenes concentration of lead sulphide complete flotation in the case of different oxidation products of galena surface in pH values from 7,0 up to 12,0. The models derived can be used as the criteria for functional units of automation systems to control and regulate the flotation process in mineral processing plants. All these should conduct to increasing of metals extraction degree with minimum chemical reagents consumption and providing good environmental protection.

Copyright © 2013 Chettibi M., and Abramov A.A. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

#### INTRODUCTION

Flotation is undoubtedly the most important and versatile mineral processing technique, and both its use and application are continually being expanded to treat greater tonnages and to cover new areas. (Wills, 2005). In modern industrial practice, flotation is characterized by its instability. The main cause of the parameters instability of metals extraction in functional plants is the changeable and not optimized physico-chemical conditions of flotation pulp, brought out by the variation of ore structure, water and reagents concentration in the pulp liquid phase during flotation process (Plaksin, 1960 and Plaksin, 1965). Settlement of this problem can be done by physico-chemical modeling of flotation systems (Abramov, 1993 and Abramov, 1977) which is conditioned by the necessity of transition from qualitative ideas to quantitative principles of flotation processes to optimize reagent conditions by means of automation and to improve the flotation technology with due regard to ecological requirements. The main point of physico-chemical modeling is the thermodynamic analysis of the flotation system (Abramov, 1977). The derived model in this case is a quantitative relationship between the concentrations of reagents in the pulp at the boundary conditions of well known (or established) reactions proceeding and the formation of either product on the mineral (Abramov, 1970). Reliability of quantitative relationship derived is verified by the results of

experimental investigations because of the metastable reactions may turn out more preferable than the most profitable ones as result of kinetic difficulties (Garrels and Christ 1964). While thermodynamic analysis of flotation systems are used the following well known relationships: the one between the equilibrium constant of reaction (K) and concentration of components ([C]) taking part in reaction; the standard free energy of reaction ( $F^0$ ) and its equilibrium constant (K) or standard electrode potential ( $E^0$ ); the potential of reaction (E), its standard electrode potential ( $E^0$ ) and equilibrium constant (K) (Abramov, 1978 Puonala, 1997, Trahar, 1983). The purpose of the present paper consists in the definition of optimal values and necessary xanthenes concentration for galena complete flotation. For that, it was studied the following: - analysis of galena surface state; electrochemical characteristics state of galena surface oxidation products; the surface state of lead xanthenes in solution and the physico-chemical models elaboration of xanthenes necessary concentration for galena flotation.

#### MATERIALS AND METHOD

The main method used in this work for computing, characterizing and modeling galena flotation system is the thermodynamic analysis method; witch is applied largely for a long time for the study of the chemical, geochemical and hydrometallurgical processes. The utility of this method in the field of mineral processing (and particular in flotation) is shown in (Abramov 1978 and Abramov 1993). This method

\*Corresponding author: Chettibi M. Annaba University, BP12- Algeria, Faculty of Earth Sciences, Mining Department, Annaba 23000, Algeria.

allowed us to define the composition of the salts liaisons, representing the minerals surfaces, to carry out physicochemical models for the processes of mineral surface interaction with the reagents, including the lawsuits of the absorptive collector layer formation, and to carry out the complete chemical state of liquid phase ionic components of floating pulp. The thermodynamic method of the analysis is based on the following equations [4]:

- Equation of the constant of balance:

$$K = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}; \quad (2.1)$$

- Equation of the relation between the free standard energy of the reaction and the constant of balance:

$$\Delta F_r^0 = \sum \Delta F_{init}^0 - \sum \Delta F_{final}^0 = R.T.\ln K; \quad (2.2)$$

Or at 25 °C  $\Delta F_r^0 = -1,364.\lg K$

- Equation of the relation between the reaction free standard energy and the potential of standard electrode:

$$\Delta F_r^0 = -n.f = 23,06.n.E^0 \quad (2.3)$$

- Equation of the relation between the reaction measured potential, the standard potential and the reaction constant of balance:

$$E = E^0 + \frac{R.T}{n.F} \ln \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} \quad (2.4)$$

Or at temperature 25 °C  $E = E^0 + \frac{0,059}{n} \log \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$

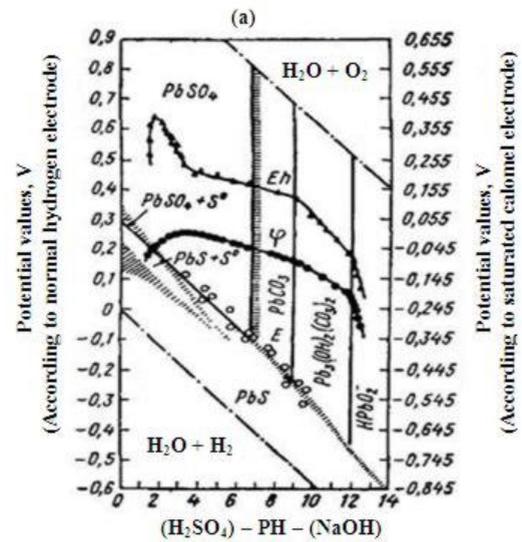
It was confirmed theoretically and experimentally in different Abramov's works (Abramov, 1977; Abramov, 1978 and Abramov, 1993) the possibility of estimating the surface quality of minerals salt, based on thermodynamic calculation. The point of this method is to create system of basic reactions of dissociation and hydrolysis of minerals in the joint solution, and resolution of the realized equations obtained on the basis of these reactions. Adding to that, the elaborate system must be supplemented by the equations of balance and the electroneutrality for the conformity of equations and unknowns quantity. While modeling the standard free energies of formation (Gibbs energies) of species and compounds were used (in Kcal/mol) after (Latimer, 1952) PbS -22,15; PbSO<sub>4</sub> -193,89; PbS<sub>2</sub>O<sub>3</sub> -134,00; Pb(OH)<sub>2</sub> -100,6; PbCO<sub>3</sub> -149,7; Pb<sup>2+</sup> -5,81; Pb(OH)<sup>+</sup> -54,08; HPbO<sub>2</sub><sup>-</sup> -81,0; S<sup>2-</sup> +22,1, HS<sup>-</sup> +3,01; H<sub>2</sub>S -6,54; SO<sub>3</sub><sup>2-</sup> -116,10; SO<sub>4</sub><sup>2-</sup> -177,34; CO<sub>3</sub><sup>2-</sup> -126,22; HCO<sub>3</sub><sup>-</sup> -140,31; H<sub>2</sub>CO<sub>3</sub> -149,0; OH<sup>-</sup> -37,595; H<sub>2</sub>O -56,69; H<sub>2</sub>SO<sub>4</sub> -177,34; after [Eliseev, 1976] Pb<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> -406,0; after (Garrels and Christ, 1964) S<sub>2</sub>O<sub>3</sub><sup>2-</sup> -127, 20.

## RESULTS AND DISCUSSIONS

### Analysis of Galena Surface State

Results of the thermodynamic analysis and experimental researches see (Figure 1, (a)) show, that in usual conditions, galena surface is represented by products of its oxidation:

PbSO<sub>4</sub> (pH = 1.6-6.07); PbCO<sub>3</sub> (pH = 6.07- 9.06); Pb<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> (pH = 9.06-12.00), at > 12 galena surface being oxidized is dissolved with formation of HPbO<sub>2</sub><sup>-</sup> and at <1,6 elementary sulfur formation (S<sup>0</sup>) was observed on naked sulphide surface (Abramov, 1978).



Note:

- O<sub>2</sub> + H<sub>2</sub>O: higher limit of water stability;

- H<sub>2</sub> + H<sub>2</sub>O: lower limit of water stability.

Fig.1. Influence of redox potential and pH values of solution on galena surface state at temperature 25° and global depression 1 atm. (dissolved carbonic acid concentration in solution = 10<sup>-5</sup>mol/l)

### Estimation of Electrochemical Characteristics State of Galena Surface and Its Oxidation Products

In order to estimate the electrochemical characteristics state of galena surface and its oxidation products was used the following reactions and equations see (Table 1): reactions of dissociation (1.1- 1.12), equations of balance (I.1 – I.7), electrode reactions (1.13 -1.16) and the equations (I.9 –I.12), particularly: for PbSO<sub>4</sub> - reactions and equations (1.2, 1.5 – 1.7, 1.10, 1.14, I.2, I.6); for PbCO<sub>3</sub> - reactions and equations (1.3, 1.5 – 1.7, 1.11- 1.15, I.6, I.7) and finally for Pb<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> - reactions and equations (1.4 – 1.7, 1.12, 1.16, I.4, I.7). From result of full chemical computation were defined equilibrium values for each product see (Figure 2), and corresponding to them the regularities of potential determining ions concentration at various values. The equilibrium values of system [product – water] make: for PbSO<sub>4</sub> – 6,23; for PbCO<sub>3</sub> – 6,26 and for Pb<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> – 6, 20. Thus, the equilibrium condition of system answers the minimal value of its free energy, so the obtained equilibrium values of systems can be considered as value of potential zero charge of oxidation product surface within galena oxidized surface. Carried out potential values of each product surface (on the basis of values of potential determining ions concentrations corresponded to them) are illustrated on Figure 3, (b). They show, that surface potentials values of minimal charge practically coincides on values with of maximal hydrophobicity and floatability of galena. Important to note, that stoichiometric anions replacement (SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, OH<sup>-</sup>) of intermediate connection on galena surface by reactions (1) or (2): (Cibulke, 1962).

Table 1. The thermodynamic characteristics (K, ΔF<sup>0</sup>, E<sup>0</sup>) reactions and equations

N <sub>2</sub> react .& equa t.	reactions and equations	K	ΔF <sup>0</sup> reaction Kcal.	E <sup>0</sup> , V.
1.1	$PbS \rightleftharpoons Pb^{2+} + S^{2-}$	$K_1=6,592.10^{-29}$	38,44	
1.2	$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$	$K_2=1,34.10^{-8}$	10,74	
1.3	$PbCO_3 \rightleftharpoons Pb^{2+} + CO_3^{2-}$	$K_3=1,11.10^{-13}$	17,67	
1.4	$Pb_3(OH)_2(CO_3)_2 \rightleftharpoons 3 Pb^{2+} + 2(OH)^- + 2CO_3^{2-}$	$K_4=2,1.10^{-45}$	60,94	
1.5	$Pb(OH)^+ \rightleftharpoons Pb^{2+} + OH^-$	$K_5=1,5.10^{-8}$	10,67	
1.6	$Pb(OH)_2^{2+} + H_2O \rightleftharpoons H^+ + Pb(OH)_2^{2+}$	$K_6=1,24.10^{-11}$	14,875	
1.7	$Pb(OH)_2^{2+} \rightleftharpoons H^+ + HPbO_2^-$	$K_7=1,2.10^{-11}$	14,896	
1.8	$HS^- \rightleftharpoons H^+ + S^{2-}$	$K_8=1,01.10^{-14}$	19,09	
1.9	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	$K_9=0,24.10^{-2}$	02,60	
1.10	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	$K_{10}=4,26.10^{-7}$	8,69	
1.11	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	$K_{11}=4,677.10^{-11}$	14,09	
1.12	$H_2O \rightleftharpoons H^+ + OH^-$	$K_w=10^{-17}$	19,60	
I.1	$[Pb^{2+}] + [Pb(OH)^+] = [S^{2-}] + [HS^-]$			
I.2	$[Pb^{2+}] + [Pb(OH)^+] + [Pb(OH)_2^{2+}] + [HPbO_2^-] = [SO_4^{2-}] + [HSO_4^-]$			
I.3	$[Pb^{2+}] + [Pb(OH)^+] = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]$			
I.4	$2[Pb^{2+}] + 2[Pb(OH)^+] + 2[Pb(OH)_2^{2+}] + 2[HPbO_2^-] = 3[CO_3^{2-}] + 3[HCO_3^-]$			
I.5	$2Pb^{2+} + Pb(OH)^+ - H^+ = 2S^{2-} + HS^- + OH^-$			
I.6	$2Pb^{2+} + Pb(OH)^+ - H^+ = 2SO_4^{2-} + HSO_4^- + HPbO_2^- + OH^-$			
I.7	$2Pb^{2+} + Pb(OH)^+ + H^+ = 2CO_3^{2-} + HCO_3^- + OH^-$			
1.13	$Pb + S^{2-} \rightleftharpoons PbS + 2e$		-44,25	-0,959
1.14	$Pb + SO_4^{2-} \rightleftharpoons PbSO_4 + 2e$		-16,55	-0,359
1.15	$Pb + CO_3^{2-} \rightleftharpoons PbCO_3 + 2e$		-23,48	-0,509
1.16	$3 Pb + 2(OH)^- + 2CO_3^{2-} \rightleftharpoons Pb_3(OH)_2(CO_3)_2 + 6e$		-78,37	-0,291
I.9	$E = -0,959 - 0,0295 \text{LOG}[S^{2-}]$			reac.1.13
I.10	$E = -0,359 - 0,0295 \text{LOG}[SO_4^{2-}]$			reac.1.14
I.11	$E = -0,509 - 0,0295 \text{LOG}[CO_3^{2-}]$			reac.1.15
I.12	$E = -0,291 - 1/3 * 0,059 (PH + \text{LOG}[CO_3^{2-}])$			reac.1.16

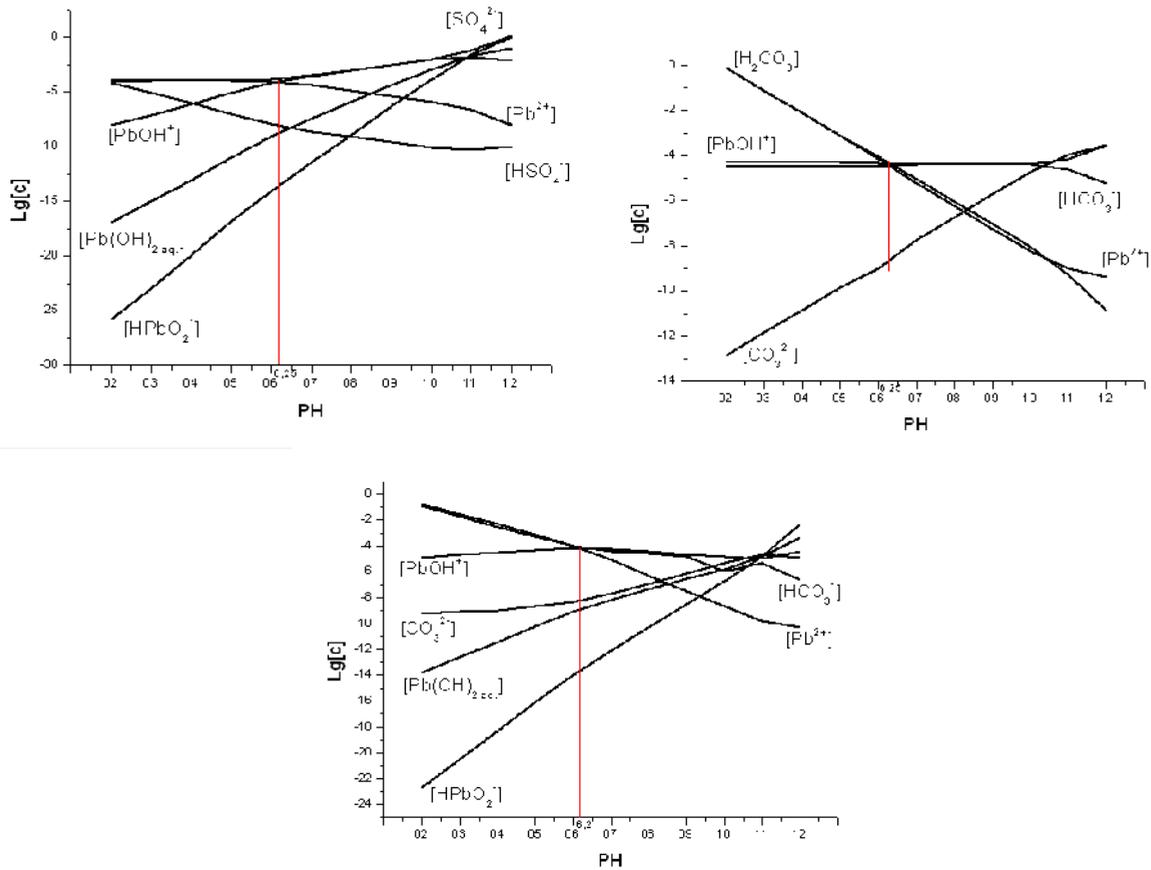
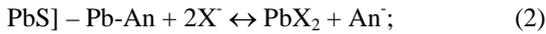


Fig.2. Influence of pH on the ions concentrations, and equilibrium pH determination in the case of different galena oxidation products: PbSO<sub>4</sub> (1); PbCO<sub>3</sub> (2); Pb<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> (3)



Where: An- anions of  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$ , equally charged with  $\text{X}^-$  anions, in result of their chemical sorption there is no change of global charge in Stern's layer, though can change the electro-kinetic potential values (in the negative side) due to layer thickness increasing by chemical sorption of xanthenes ions, having the much more size, in comparison with inorganic ions.

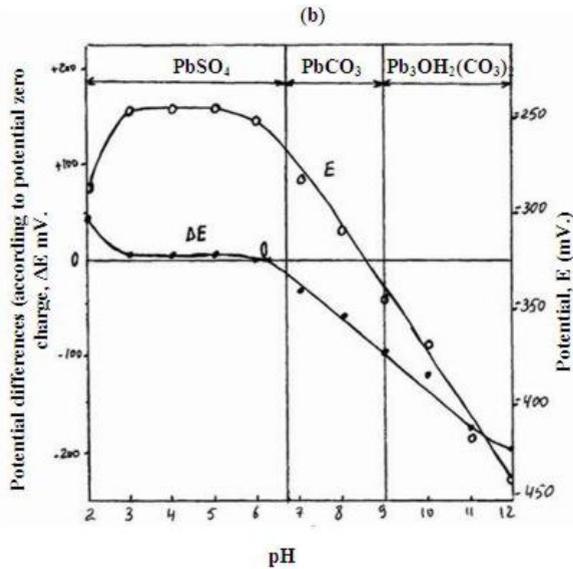


Fig.3. pH influence on potential values ( ) and potential differences ( ) of galena oxidized surface (fig. b) at interval of following components formation:  $\text{PbSO}_4$ ,  $\text{PbCO}_3$  and  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$

### Lead Xanthenes Surface Behavior In Solution and Its Equilibrium pH

For studying lead xanthenes surface state ( $\text{PbX}_2$ ) in a solution, an equations system has been made from expressions of equilibrium constant of dissociation reactions (2.1 - 2.6), the equations of balance (II.1) and electro neutrality (II.2), electrode reactions (2.7, for butyl and ethyl xanthenes) and the equations corresponding to them (II.3, II.4) (see Table. 2).

From result of full chemical calculation was determined the equilibrium values of lead xanthenes and variation regularities of ions determining potential concentration according to them. It was found, that balance value of system « Lead xanthenes - water » makes: for  $\text{PbX}_2$  but. - 6,3 and for  $\text{PbX}_2$  ethyl. - 6,15 (Chettibi, 2002). Since, the system equilibrium condition answers the minimal value of its free energy, so the obtained system equilibrium pH values can be considered as potential values of the minimal charge of lead xanthenes surface. Practically, potential value of surface minimal charge of sulphide minerals coincides by values with corresponding maximal hydrophobicity and floatability of galena, that confirms results of lead xanthenes surface state calculation, as values maximal floatability of galena and equilibrium of lead xanthenes surface are similar and equal 6,0. Thus, the obtained results testify that at potentials, answering minimal charge on galena surface floats optimum structure collector sorption layer, consisting from both kind of sorption; chemically fixed xanthenes and physically adsorbed dexanthogenes (Cibulke, 1962). Chemically fixed collector insures the necessary hydrophobicity of mineral surface and the thermodynamic possibility of its fastening on bubbles. Physically adsorbed collector (dexanthogenes) plays role of kinetic functions at flotation as providing effective destruction of hydro-layers between bubble and particle and hardening of contact bubble-particle. In results effective flotation could be provided (Abramov, 1993). Conformity of optimal value at flotation to value of minimal charge potential of floating mineral surface is caused by the following:

- insuring maximal surface hydrophobicity as consequence of its zero charge (it means its no polar states), and collector chemical sorption, which no polar radicals are directed towards the side of liquid phase;
- guarantee at a surface zero charge optimal conditions of physical adsorption of dexanthogenes uncharged molecules, carrying out kinetic functions while fastening and flotation of mineral (Abramov, 1993).

### Physico-chemical Modeling of Xanthenes Concentration Necessary for Galena Flotation

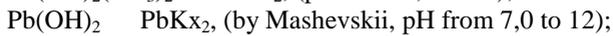
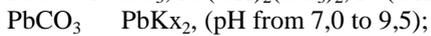
Galena sulfide surface in contacted solutions to atmosphere will rather quickly be oxidized. Because of sharp reduction of sulfide ions concentration in conditions of oxidation and

Table 2. The thermodynamic characteristics ( $K$ ,  $\Delta F^0$ ,  $E^0$ ) reactions and equations

№ react. & equation	reactions and equations	K	$\Delta F^0$ reaction Kcal.	$E^0$ , V.
2.1	$\text{PbX}_2^{\text{but}} \leftrightarrow \text{Pb}^{2+} + 2\text{X}^-$	$1,35 \cdot 10^{-19}$		-0,100
2.2	$\text{PbX}_2^{\text{ethyl}} \leftrightarrow \text{Pb}^{2+} + 2\text{X}^-$	$1,7 \cdot 10^{-7}$		-0,037
2.3	$\text{Pb}(\text{OH})^+ \leftrightarrow \text{Pb}^{2+} + \text{OH}^-$	$1,5 \cdot 10^{-8}$	10,67	
2.4	$\text{Pb}(\text{OH})^+ + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{Pb}(\text{OH})_2^{\text{ad}}$	$1,26 \cdot 10^{-11}$		
2.5	$\text{Pb}(\text{OH})_2^{\text{ad}} \leftrightarrow \text{H}^+ + \text{HPbO}_2^-$	$1,2 \cdot 10^{-11}$		
2.6	$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	$K_w = 10^{-14}$	19,095	
2.7	$2\text{X}^- \leftrightarrow \text{X}_2 + 2\text{e}^-$			
II.1	$2[\text{Pb}^{2+}] + 2[\text{Pb}(\text{OH})^+] + 2[\text{Pb}(\text{OH})_2^{\text{ad}}] + 2[\text{HPbO}_2^-] = [\text{X}^-]$			
II.2	$2\text{Pb}^{2+} + \text{Pb}(\text{OH})^+ + \text{H}^+ = \text{X}^- + \text{HPbO}_2^- + \text{OH}^-$			
II.3	$E_1 = -0,100 - 0,059 \log[\text{X}_{\text{butyl}}^-]$			r. 2.7
3.11	$E_2 = -0,037 - 0,059 \log[\text{X}_{\text{ethyl}}^-]$			r. 2.7

system aspiration of preserving solubility product of PbS, concentration of  $Pb^{2+}$  in solution will increase till its value will not be enough for the creation of lead corresponding oxidized combinations. Later,  $Pb^{2+}$  concentration will be supervised by product of the created oxidation products solubility (Abramov, 1978). The necessary concentration of xanthenes ions  $[X^-]$  has been determined According to equilibrium condition: « oxidation product lead xanthenes( $PbX_2$ ) », it guaranteed the  $PbX_2$  formation while  $X^-$  ions direct interaction with galena sulfide oxidized surface, and as available oxidation product on its surface. In usual conditions at value from 7 up to 12, final oxidation products of galena are  $PbCO_3$  or  $Pb(OH)_2(CO_3)_2$ . (Abramov, 1978; Abramov, 1973).

In the carried out calculation, four cases of sulfur oxidation has been examined, including the elementary sulfur ( $S^0$ ),  $S_2O_3^{2-}$ ,  $SO_3^{2-}$  and  $SO_4^{2-}$ . Besides were taken into account the following equilibrium reactions:



2;

The thermodynamic potential of sulfide minerals surfaces in the absence of the collector solution can be defined by the ions concentration ratio using the equation (2.4). In the presence of collector in solution, xanthenes ions will be adsorbed on the mineral surface, creating  $Me - X$ . In result, the  $X^-$  ions become the potential determining ions. Thus the mineral surface potential will be described by the following equation:

$$E = E_0 - \frac{0,059}{n} \log[X^-];$$

Xanthenes ions will compete with anions on the mineral surface. As we know, at mineral surface transition from one state to another, surfaces potentials will be equable (Buckley, Woods, 1997, Bushel, 1965, Chettibi, 2002). So, quantitative values of xanthenes necessary concentration can be determined according to the equality  $E = E_1$ , allowing calculate  $[X^-] = f(\dots)$ . The further comparison of calculated and experimental results allows defining the xanthenes necessary concentration and factors influencing on its value. Quantitative values of xanthenes necessary concentration were defined on the basis of electrode reactions (2.1 – 2.17) and corresponding them equations (II.1 - II.19), see Table 3. During calculations were taken on account four equilibrium conditions of galena oxidation products with xanthenes.

Table 3. Thermodynamic characteristics ( $E^0$ ,  $E$ ) reactions and equations

react. and equat.	Reaction and equations	$E^0$ , V	$E$ , V
2.1	$PbS + CO_3^{2-} \rightleftharpoons PbCO_3 + S^0 + 2e$	-1,38	-0,03
II.1	$E_1 = -0,03 - 1/2 \cdot 0,059 \lg[CO_3^{2-}]$		
2.2	$3PbS + 2CO_3^{2-} + 2H_2O \rightleftharpoons Pb_3(OH)_2(CO_3)_2 + 3S^0 + 2H^+ + 6e$	+26,29	+0,190
II.2	$E_2 = +0,190 - 1/3 \cdot 0,059 pH - 1/3 \cdot 0,059 \lg[CO_3^{2-}]$		
2.3	$2PbS + 2CO_3^{2-} + 3H_2O \rightleftharpoons 2PbCO_3 + S_2O_3^{2-} + 6H^+ + 8e$	+32,09	+0,174
II.3	$E_3 = +0,174 + 1/8 \cdot 0,059 \lg[S_2O_3^{2-}] - 3/4 \cdot 0,059 pH - 1/4 \cdot 0,059 \lg[CO_3^{2-}]$		
2.4	$6PbS + 4CO_3^{2-} + 13H_2O \rightleftharpoons Pb_3(OH)_2(CO_3)_2 + 3S_2O_3^{2-} + 22H^+ + 24e$	+156,6	+0,283
II.4	$E_4 = +0,283 + 1/8 \cdot 0,059 \lg[S_2O_3^{2-}] - 11/12 \cdot 0,059 pH - 1/6 \cdot 0,059 \lg[CO_3^{2-}]$		
2.5	$PbS + 3H_2O + CO_3^{2-} \rightleftharpoons PbCO_3 + SO_3^{2-} + 6H^+ + 6e$	+44,55	+0,322
II.5	$E_5 = +0,322 + 1/6 \cdot 0,059 \lg[SO_3^{2-}] - 0,059 pH - 1/6 \cdot 0,059 \lg[CO_3^{2-}]$		
2.6	$3PbS + 11H_2O + 2CO_3^{2-} \rightleftharpoons Pb_3(OH)_2(CO_3)_2 + 3SO_3^{2-} + 20H^+ + 18e$	+163,9	+0,395
II.6	$E_6 = +0,395 + 1/6 \cdot 0,059 \lg[SO_3^{2-}] - 10/9 \cdot 0,059 pH - 1/9 \cdot 0,059 \lg[CO_3^{2-}]$		
2.7	$PbS + 4H_2O + CO_3^{2-} \rightleftharpoons PbCO_3 + SO_4^{2-} + 8H^+ + 8e$	+40,03	+0,217
II.7	$E_7 = +0,217 + 1/8 \cdot 0,059 \lg[SO_4^{2-}] - 0,059 pH - 1/8 \cdot 0,059 \lg[CO_3^{2-}]$		
2.8	$3PbS + 14H_2O + 2CO_3^{2-} \rightleftharpoons Pb_3(OH)_2(CO_3)_2 + 3SO_4^{2-} + 26H^+ + 24e$	+149,9	+0,271
II.8	$E_8 = +0,271 + 1/8 \cdot 0,059 \lg[SO_4^{2-}] - 13/12 \cdot 0,059 pH - 1/12 \cdot 0,059 \lg[CO_3^{2-}]$		
2.9	$PbS + 2H_2O \rightleftharpoons Pb(OH)_2 + S^0 + 2H^+ + 2e$	+34,9	+0,757
II.9	$E_9 = +0,757 - 0,059 pH$		
2.10	$2PbS + 7H_2O \rightleftharpoons Pb(OH)_2 + S_2O_3^{2-} + 10H^+ + 8e$	+104,6	+0,567
II.10	$E_{10} = +0,567 + 1/8 \cdot 0,059 \lg[S_2O_3^{2-}] - 5/4 \cdot 0,059 pH$		
2.11	$PbS + 6H_2O \rightleftharpoons Pb(OH)_2 + SO_4^{2-} + 10H^+ + 8e$	+76,19	+0,413
II.11	$E_{11} = +0,413 + 1/8 \cdot 0,059 \lg[SO_4^{2-}] - 5/4 \cdot 0,059 pH$		

Comparing calculation results with experimental data of different concentrating plants (Abramov, 1978), it has been established, that definitions of xanthenes necessary concentration at equilibrium conditions [PbS Pb(OH)<sub>2</sub> and PbS PbX<sub>2</sub>], and also [PbS Pb(OH)<sub>2</sub> and X<sup>-</sup> X<sub>2</sub>] are impossible, because calculation results do not coincide with experimental data (Fig. 4.a and 5.d). It contradicts Mashevskii's results. Besides lead hydroxide in open system couldn't be formed, as at any values they supersede in lead carbonates.

$$\log [X^-]_{nec.} = -6.66 + 1/3.pH + 1/2.lg[CO_3^{2-}] \tag{4}$$

These last dependences represent quantitative physico-chemical models of lead sulfide flotation process. The elaborated models (3) and (4) can be used as a task of functional block in automation system of control and regulation flotation process in the plants.

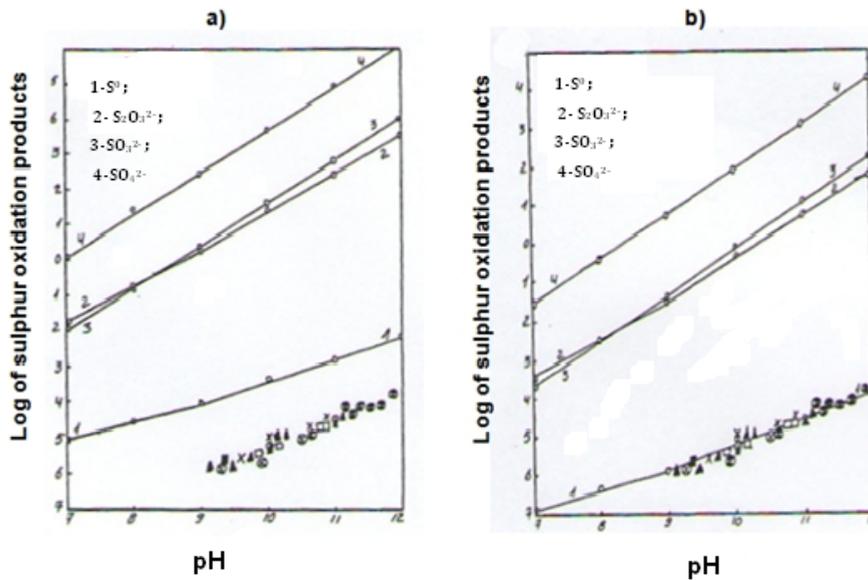


Fig. 4 - Influence of pH on butyl xanthenes necessary concentration in galena flotation: [X<sub>2</sub>] = 10<sup>-5</sup> (a); 3,18.10<sup>-4</sup> (b). In equilibrium conditions of: PbS PbCO<sub>3</sub>; Pb<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> and X<sup>-</sup> X<sub>2</sub>. (experimental results were taken from different experiences affected on galena of different deposits [2<sup>nd</sup> soviet deposit, Treptcha Yugoslavian deposit, Madjarovo Bulgarian deposit, bepezovskii Russian deposit], [4], [Abramov, 1978]).

Fig. 4 - Influence of pH on butyl xanthenes necessary concentration in galena flotation: [X<sub>2</sub>] = 10<sup>-5</sup> (a); 3,18.10<sup>-4</sup> (b). In equilibrium conditions of: PbS PbCO<sub>3</sub>; Pb<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> and X<sup>-</sup> X<sub>2</sub>. (experimental results were taken from different experiences affected on galena of different deposits [2<sup>nd</sup> soviet deposit, Treptcha Yugoslavian deposit, Madjarovo Bulgarian deposit, bepezovskii Russian deposit], (Abramov, 1978)). However, calculations results at equilibrium conditions PbS PbCO<sub>3</sub>; Pb<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> and X<sup>-</sup> X<sub>2</sub> coincide experimental results only in case of elementary sulfur (S<sup>0</sup>) formation at dixanthenes concentration equal 3,18.10<sup>-4</sup> mol/l, assuring the formation of lead xanthenes on mineral surface with elementary sulfur sharing out (see fig. 4.b), and similar results at equilibrium condition PbS PbCO<sub>3</sub>; Pb<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> and PbS PbX<sub>2</sub>. (see Fig. 5.c). Thus calculations results completely coincide with experimental data independently on which product of sulfur oxidation is formed in solution. It means, no matter the products of sulfur oxidation are, they have no influence on the transition of galena oxidized surface to lead xanthenes as also proved (Abramov, 1978).

Consequently, on the basis of carried out calculations results were obtained the following quantitative dependences:

a/ in condition of lead carbonate formation PbCO<sub>3</sub>, from 7,0 up to 9,0:

$$\log [X^-]_{neces.} = -2,98 + 1/2.lg[CO_3^{2-}] \tag{3}$$

b/ in condition of lead hydro carbonate formation Pb<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>, from 9,0 up to 12:

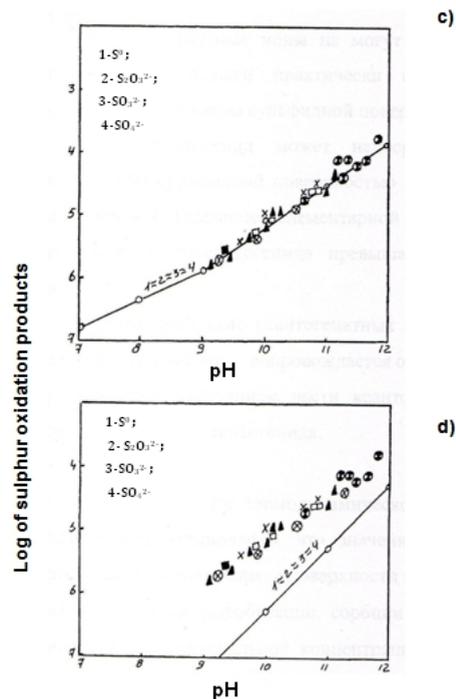


Fig.5 - Influence of pH on butyl xanthenes necessary concentration in galena flotation in equilibrium conditions of: PbS PbCO<sub>3</sub>; Pb<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> and PbS PbX<sub>2</sub> ( C ); PbS Pb(OH)<sub>2</sub> and PbS PbX<sub>2</sub> ( d ). (experimental results were taken from different experiences affected on galena of different deposits [2<sup>nd</sup> soviet deposit, Treptcha Yugoslavian deposit, Madjarovo Bulgarian deposit, bepezovskii Russian deposit], [4] (Abramov, 1978)

In result we can obtain maximum technological indexes values of galena selection. Values of butyl xanthenes ions concentration, necessary for lead butyl xanthenes creation on galena surface make:  $1,2 \cdot 10^{-7}$  at  $-7$ ;  $4,0 \cdot 10^{-7}$  at  $-8$ ;  $1,2 \cdot 10^{-6}$  at  $-9$ ;  $8,5 \cdot 10^{-6}$  at  $-10$ ;  $2,9 \cdot 10^{-5}$  at  $-11$ ;  $1,3 \cdot 10^{-4}$  at  $-12$ .

## Conclusions

From results of thermodynamic analysis and experimental data we can conclude the following moments:

- Optimum pH values for galena flotation answer surface potential of minimal charge, guaranteeing the formation of collector optimum sorption coverings structure.
- value, answering to surface potential of zero or minimal charge floating mineral can be defined as a result of thermodynamic calculation of the surface state in suggested conditions of flotation.
- Equilibrium value corresponding to minimum charge potential of lead xanthenes surface, presents the most important condition of maximum hydrophobicity, dextranthenes sorption and mineral floatability at minimum collector concentration in solution. The given value makes: in the case of butyl xanthenes 6,3; and ethyl xanthenes 6,15.
- Dependences of minimal necessary xanthenes concentration on pH values in pulp at galena flotation, representing quantitative physico-chemical models of lead sulfide flotation process, can be used as task of functional block in automation system for controlling and regulating flotation process at concentrating plants. That will conduct to increasing of metals extraction degree, decreasing chemical reagents consumption and providing good environmental protection.

## Acknowledgements

The work described in this paper forms part of a research program of Mineral Processing Department, Moscow Mining State University, Russia. The author is grateful to the Head of M. P, Department and its staff for advice and for helping to achieve this work, and the best thanks are for Pr. Abramov A. A. for his assistance and contribution in this work.

## REFERENCES

Abramov A. A. 1970. Principles of flotation of sulphide minerals of lead, copper and iron in the presence of sulphide ions. *Oborashenie rud*, (1-2), Moscow, Russia.

Abramov A. A. 1977. Physicochemical modelling of flotation systems, Moscow, ed."MISIS", p. 110, Russia.

Abramov A. A. 1983. Technology of nonferrous metals ores processing, Moscow, ed. "Nedra".

Abramov A. A., 1973. Investigation of the action of reagents and optimization of their concentration in the flotation pulp. X International Mineral processing Congress. London, P. 633-652.

Abramov A. A., 1978. Theoretical Principles of Optimization of sulphide ores selective flotation. Moscow, Nedra.

Abramov A. A., 1993. Mineral processing by using flotation methods. Nedra, Moscow.

Abramov A. A., Leonov S. B., Sorokin N. M. 1982. Chemistry of flotation systems, Moscow, ed. "Nedra".

Buckley A. N., Woods R., 1997. Chemio-sorption- the thermodynamically favored process in the interaction of thiol collectors with sulphide minerals. *Int. J. Miner. Process.* 51, p. 15-26.

Bushel C. H. G., 1965. On the action of Xanthenes in flotation. *Canadian Mining Metallurgical Bulletin*, V. 58, N<sup>0</sup>642, p.1083.

Chettibi M., 2002. Optimization of Lead and Zinc Mineral Sulfide flotation. PhD Thesis; Moscow Mining University. Russia.

Cibulke I., 1962. Virkum moznosti rirení flotace sirniki pomosi mereni hodnot zbytkove koncentrace. *Celostatni Konference redneho hornistvi a upravnictvi*. Praha, p. 39.

Eliseev N. I., Kirbitova N. V., Levina L. A., 1976. Questions of formation of basic metal xanthenes. *Izv. Vyssh. Ucheb. Zaved. Gorn. Zh.* 2. Moscow, Russia.

Erikson G. A., 1979. A logarithm for the computation of aqueous multicomponent, multiphase equilibria. *Anal. Chim. Acta*.

Finkelstein N. P., Harris P. J., 1975. Interactions between sulphide minerals and xanthenes. The formation of MTC at galena and pyrite surfaces. *Int. J. Miner. Process.*

Forsberg K. S. E., Antti B. M., Pallson B., 1984. Computer assisted calculations of the thermodynamic equilibria chalcopyrite – ethylxanthate system. In : Jones M. J. and Oblatt R. editions, *Reagents in the mineral industry*. IMM, London.

Fuerstenau M. C., Natalie C. A., et al, 1990. Xanthate adsorption on selected sulphides in the virtual absence and presence of oxygen. Parts 1 and 2, *Int. J. Miner. Process.*

Garrels R. M., Christ C. L., 1964. *Solutions, Minerals and Equilibria*. Freeman, San Francisco, California, USA.

Heifetz V. L., Krasikov B. S., 1959. Influence of surface active substances on kinetics of certain cations discharge. *Scientific notes of LGU*. 262, p.3-30.

Khan G. A., 1965. Distribution of xanthenes concentration remainder in flotation cycle. *Tsvetnaya metalurguiya*, N<sup>0</sup>24, p. 17-19.

Latimer W. M., 1952. *Oxidation potentials*. New York, Prentice and Hall, 2<sup>nd</sup> edition.

Melik-Gaykazian V. I., Abramov A. A., 1990. Investigation methods of flotation process. Moscow, Nedra.

Montalti M., 1991. Australian mineral industries research association. Final report, 1.

Plaksin I. N., 1960. Evolution of mineral processing theory and technique. *CIIN CM*, N<sup>0</sup>1, p. 157-162.

Plaksin I. N., 1965. Xanthenes in liquid phase pulp. Moscow, Nauka, P. 26-48.

Puonala M., Heimala S., Jounela S., 1997. Different aspects of using electrochemical potential measurements in mineral processing. *Int. J. Miner. Process.* 51, p. 97-110.

Trahar w., 1983. The influence of pulp potential in sulphide flotation In: Jones M. H. and Woodcock J. T. editions, *Principle of mineral flotation*. Wark symposium Austr. Inst. Min. Metal.

Wills B. A., 2005. *Mineral Processing Technology*. London, Elsevier edition, V.7, p. 267.