

*Full Length Research Paper*

# Modeling of flotation system of galena as way to process improvement and environment protection

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Accepted 02 May, 2012

**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, we've obtained quantitative physico-chemical 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. Physico-chemical 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.**

**Keywords:** Flotation, Galena, Thermodynamic analysis, Modeling, Environment.

## 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; Plaksin, 1965; Khan, 1965).

Settlement of this problem can be done by physico-chemical modeling of flotation systems (Abramov, 1977,

1993) 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, 1979).

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, 1964).

While thermodynamic analysis of flotation systems are

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used the following well known relationships: the one between the equilibrium constant of reaction (K) and concentration of components ([ ]) taking part in reaction; the standard free energy of reaction ( $\Delta F^0$ ) 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).

The purpose of the present paper consists in the definition of optimal pH 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; which 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, 1993). This method 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 (Abramov, 1979):

- 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:

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

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

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

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

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

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

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, 1978, 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 W. M., 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 N. I., et al. 1976] Pb<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> -406,0; after [Garrels R. M., et al., 1964] S<sub>2</sub>O<sub>3</sub><sup>2-</sup> -127,20.

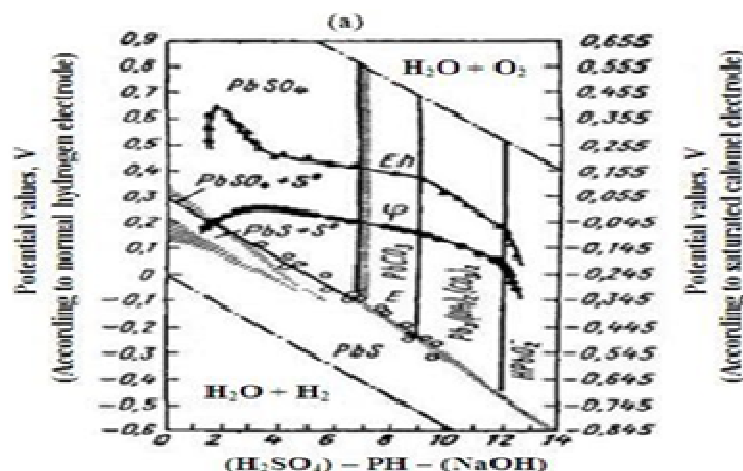
## RESULTS AND DISCUSSIONS

### 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 pH > 12 galena surface being oxidized is dissolved with formation of HPbO<sub>2</sub><sup>-</sup> and at pH<1,6 elementary sulfur formation (S<sup>0</sup>) was observed on naked sulphide surface (Abramov, 1978).

### 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 (1.1 – 1.7), electrode reactions (1.13 -1.16) and the equations (1.9 –1.12), particularly: for PbSO<sub>4</sub> - reactions



Note:

- $O_2 + H_2O$ : higher limit of water stability;
- $H_2 + H_2O$ : lower limit of water stability.

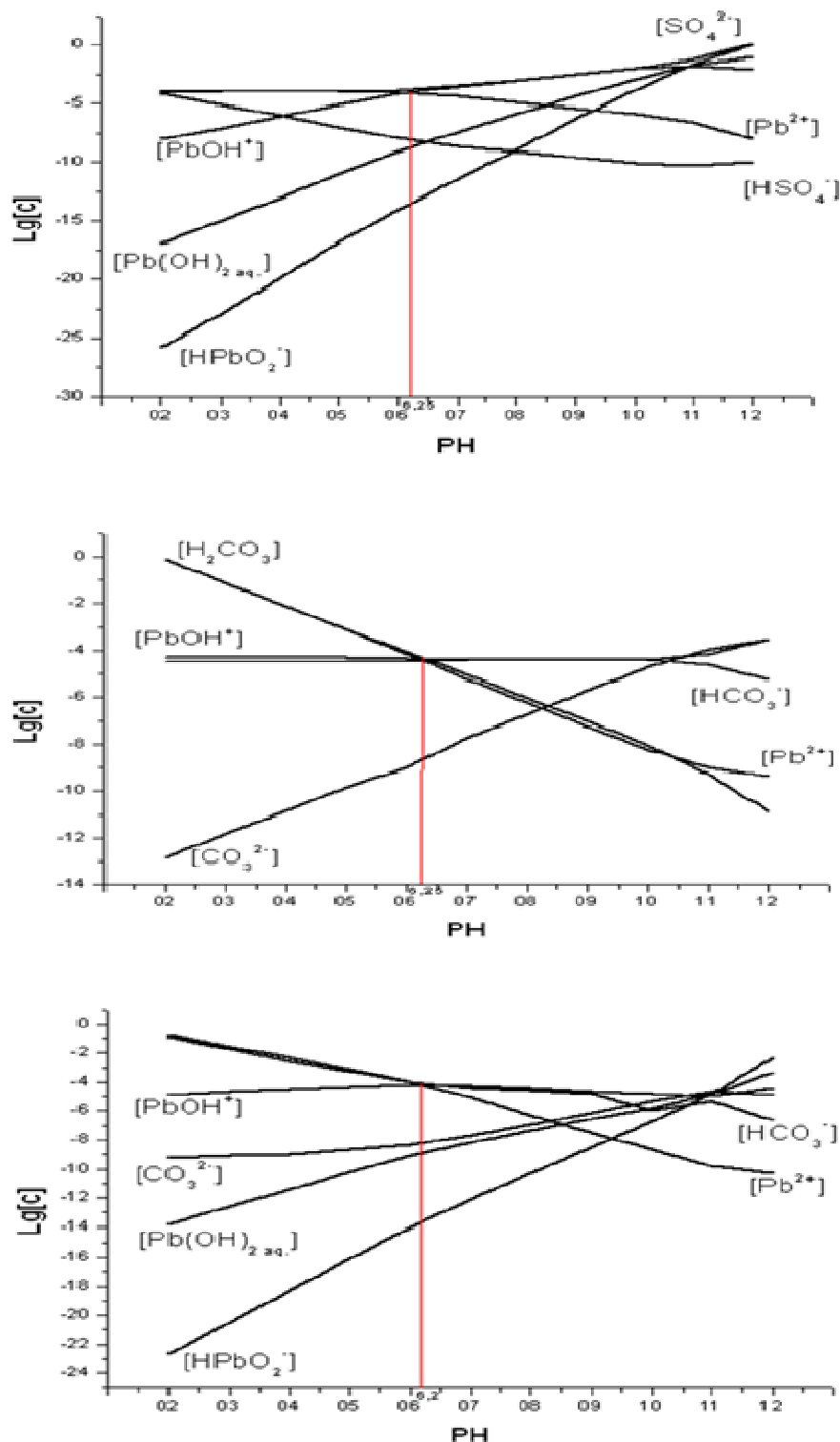
**Figure 1.** Influence of redox potential and pH values of solution on galena surface state at temperature 25°C and global depression 1 atm. (dissolved carbonic acid concentration in solution = 10<sup>-5</sup> mol/l).

**Table 1.** The thermodynamic characteristics (K,  $\Delta F^0$ ,  $E^0$ ) reactions and equations.

Nº react. & equat.	reactions and equations	K	$\Delta F^\circ$ reaction Kcal.	$E^\circ$ , V.
1.1	$PbS \rightleftharpoons Pb^{2+} + S^{2-}$	$K_1 = 6,592 \cdot 10^{-29}$	38,44	
1.2	$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$	$K_2 = 1,34 \cdot 10^{-8}$	10,74	
1.3	$PbCO_3 \rightleftharpoons Pb^{2+} + CO_3^{2-}$	$K_3 = 1,11 \cdot 10^{-13}$	17,67	
1.4	$Pb_3(OH)_2(CO_3)_2 \rightleftharpoons 3 Pb^{2+} + 2(OH)^- + 2CO_3^{2-}$	$K_4 = 2,1 \cdot 10^{-45}$	60,94	
1.5	$Pb(OH)^+ \rightleftharpoons Pb^{2+} + OH^-$	$K_5 = 1,5 \cdot 10^{-8}$	10,67	
1.6	$Pb(OH)_2^{aq} + H_2O \rightleftharpoons H^+ + Pb(OH)_2^{aq}$	$K_6 = 1,24 \cdot 10^{-11}$	14,875	
1.7	$Pb(OH)_2^{aq} \rightleftharpoons H^+ + HPbO_2^-$	$K_7 = 1,2 \cdot 10^{-11}$	14,896	
1.8	$HS^- \rightleftharpoons H^+ + S^{2-}$	$K_8 = 1,01 \cdot 10^{-14}$	19,09	
1.9	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	$K_9 = 0,24 \cdot 10^{-2}$	02,60	
1.10	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	$K_{10} = 4,26 \cdot 10^{-7}$	8,69	
1.11	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	$K_{11} = 4,677 \cdot 10^{-11}$	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	$[Pb^{2+}] + [Pb(OH)^+] + [Pb(OH)_2^{aq}] + [HPbO_2^-] = [SO_4^{2-}] + [HSO_4^-]$			
I.3	$[Pb^{2+}] + [Pb(OH)^+] = [CO_3^{2-}] + [HCO_3^-] - [H_2CO_3]$			
I.4	$2[Pb^{2+}] + 2[Pb(OH)^+] + 2[Pb(OH)_2^{aq}] + 2[HPbO_2^-] = 3[CO_3^{2-}] + 3[HCO_3^-]$			
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

and equations (1.2, 1.5 – 1.7, 1.10, 1.14, 1.2, 1.6); for  $\text{PbCO}_3$  - reactions and equations (1.3, 1.5 – 1.7, 1.11-

1.15, 1.6, 1.7) and finally for  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$  - reactions and equations (1.4 – 1.7, 1.12, 1.16, 1.4, 1.7).

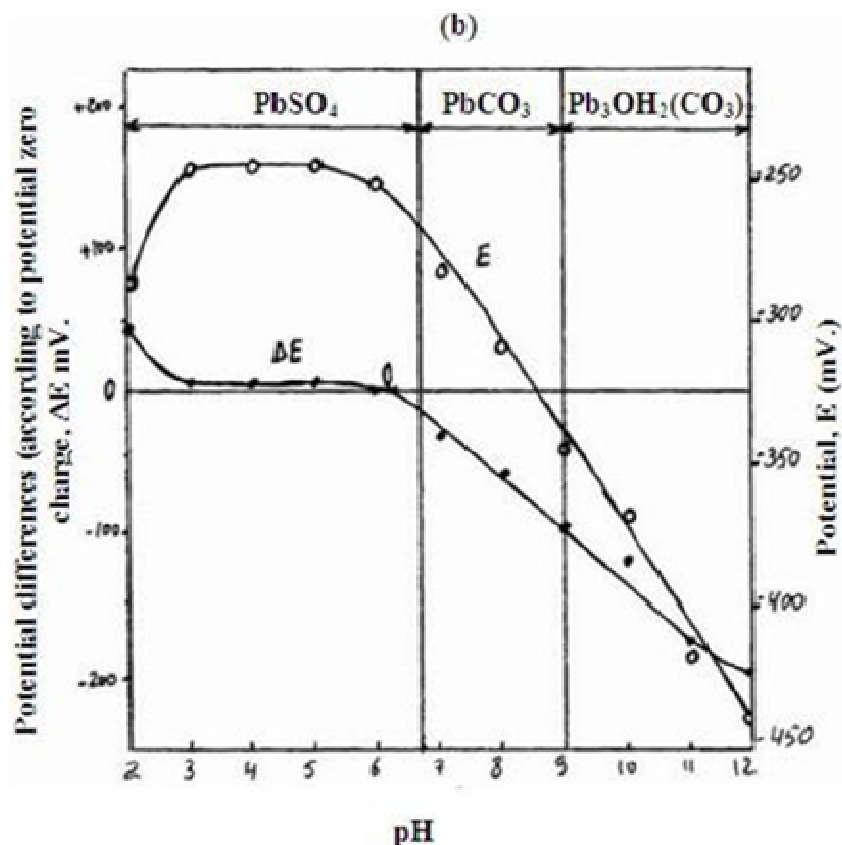


**Figure 2.** Influence of pH on the ions concentrations, and equilibrium pH determination in the case of different galena oxidation products:  $\text{PbSO}_4$  (1);  $\text{PbCO}_3$  (2);  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$  (3)

From result of full chemical computation were defined pH equilibrium values for each product see (figure 2), and corresponding to them the regularities of potential deter-

mining ions concentration at various pH values.

The pH equilibrium values of system (product – water) make: for  $\text{PbSO}_4$  – 6, 23; for  $\text{PbCO}_3$  – 6, 26 and for

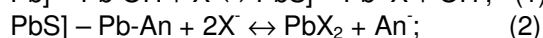
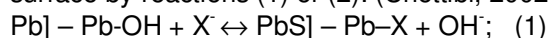


**Figure 3.** pH influence on potential values ( $E$ ) and potential differences ( $\Delta E$ ) of galena oxidized surface (fig. b) at interval of following components formation:  $\text{PbSO}_4$ ,  $\text{PbCO}_3$  and  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ .

$\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2 - 6,20$ . Thus, the equilibrium condition of system answers the minimal value of its free energy, so the obtained pH 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 pH values with pH of maximal hydrophobicity and floatability of galena. Important to note, that stoichiometric anions replacement ( $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ ) of intermediate connection on galena surface by reactions (1) or (2): (Chettibi, 2002).



Where:  $\text{An}^-$  - 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.

### 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 pH values of lead xanthenes and variation regularities of ions determining potential concentration according to them. It was found, that balance pH value of system « Lead xanthenes - water » makes: for  $\text{PbX}_{2 \text{ but.}}$  - 6,3 and for  $\text{PbX}_{2 \text{ ethyl.}}$  - 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

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

N <sup>o</sup> react & equa t.	reactions and equations	K	$\Delta F^0$ reactio n Kcal.	$E^0$ , V.
2.1	$PbX_2_{\text{but}} \leftrightarrow Pb^{2+} + 2X^-$	$1,35 \cdot 10^{-19}$		-0,100
2.2	$PbX_2_{\text{atrvl}} \leftrightarrow Pb^{2+} + 2X^-$	$1,7 \cdot 10^{-7}$		-0,037
2.3	$Pb(OH)^+ \leftrightarrow Pb^{2+} + OH^-$	$1,5 \cdot 10^{-8}$	10,67	
2.4	$Pb(OH)^+ + H_2O \leftrightarrow H^+ + Pb(OH)_2_{\text{ss}}$	$1,26 \cdot 10^{-11}$		
2.5	$Pb(OH)_2_{\text{ss}} \leftrightarrow H^+ + HPbO_2^-$	$1,2 \cdot 10^{-11}$		
2.6	$H_2O \leftrightarrow H^+ + OH^-$	$K_w = 10^{-14}$	19,095	
2.7	$2X^- \leftrightarrow X_2 + 2e^-$			
II.1	$2[Pb^{2+}] + 2[Pb(OH)^+] + 2[Pb(OH)_2_{\text{ss}}] + 2[HPbO_2^-] = [X^-]$			
II.2	$2 Pb^{2+} + Pb(OH)^+ + H^+ = X^- + HPbO_2^- + OH^-$			
II.3	$E_1 = -0,100 - 0,059 \log[X^-_{\text{butvl}}]$			r. 2.7
3.11	$E_2 = -0,037 - 0,059 \log[X^-_{\text{atrvl}}]$			r. 2.7

minimal charge of lead xanthenes surface.

Practically, potential value of surface minimal charge of sulphide minerals coincides by pH values with pH corresponding maximal hydrophobicity and floatability of galena, that confirms results of lead xanthenes surface state calculation, as pH values maximal floatability of galena and equilibrium pH 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 (Chettibi, 2002).

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 pH 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 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  $\leftrightarrow$  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 pH value from 7 up to 12, final oxidation products of galena are  $PbCO_3$  or  $Pb(OH)_2(CO_3)_2$ . (Abramov, 1978).

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:  $PbS \leftrightarrow PbCO_3$ ,  $Pb(OH)_2(CO_3)_2$ ,  $Pb(OH)_2$ ;

**Table 3.** Thermodynamic characteristics ( $\Delta F^0$ ,  $E^0$ ) reactions and equations.

No. react. and equat.	Reaction and equations	$\Delta F^0$ ReactKcal.	$E^0$ , V
2.1	$\text{PbS} + \text{CO}_3^{2-} \rightleftharpoons \text{PbCO}_3 + \text{S}^0 + 2\text{e}$	-1,38	-0,03
II.1	$E_1 = -0,03 - \frac{1}{2} \cdot 0,059 \lg[\text{CO}_3^{2-}]$		
2.2	$3\text{PbS} + 2\text{CO}_3^{2-} + 2\text{H}_2\text{O} \rightleftharpoons \text{Pb}_3(\text{OH})_2(\text{CO}_3)_2 + 3\text{S}^0 + 2\text{H}^+ + 6\text{e}$	+26,29	+0,190
II.2	$E_2 = +0,190 - 1/3 \cdot 0,059 \text{pH} - 1/3 \cdot 0,059 \lg[\text{CO}_3^{2-}]$		
2.3	$2\text{PbS} + 2\text{CO}_3^{2-} + 3\text{H}_2\text{O} \rightleftharpoons 2\text{PbCO}_3 + \text{S}_2\text{O}_3^{2-} + 6\text{H}^+ + 8\text{e}$	+32,09	+0,174
II.3	$E_3 = +0,174 + 1/8 \cdot 0,059 \lg[\text{S}_2\text{O}_3^{2-}] - \frac{3}{4} \cdot 0,059 \text{pH} - \frac{1}{4} \cdot 0,059 \lg[\text{CO}_3^{2-}]$		
2.4	$6\text{PbS} + 4\text{CO}_3^{2-} + 13\text{H}_2\text{O} \rightleftharpoons \text{Pb}_3(\text{OH})_2(\text{CO}_3)_2 + 3\text{S}_2\text{O}_3^{2-} + 22\text{H}^+ + 24\text{e}$	+156,6	+0,283
II.4	$E_4 = +0,283 + 1/8 \cdot 0,059 \lg[\text{S}_2\text{O}_3^{2-}] - 11/12 \cdot 0,059 \text{pH} - 1/6 \cdot 0,059 \lg[\text{CO}_3^{2-}]$		
2.5	$\text{PbS} + 3\text{H}_2\text{O} + \text{CO}_3^{2-} \rightleftharpoons \text{PbCO}_3 + \text{SO}_3^{2-} + 6\text{H}^+ + 6\text{e}$	+44,55	+0,322
II.5	$E_5 = +0,322 + 1/6 \cdot 0,059 \lg[\text{SO}_3^{2-}] - 0,059 \text{pH} - 1/6 \cdot 0,059 \lg[\text{CO}_3^{2-}]$		
2.6	$3\text{PbS} + 11\text{H}_2\text{O} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Pb}_3(\text{OH})_2(\text{CO}_3)_2 + 3\text{SO}_3^{2-} + 20\text{H}^+ + 18\text{e}$	+163,9	+0,395
II.6	$E_6 = +0,395 + 1/6 \cdot 0,059 \lg[\text{SO}_3^{2-}] - 10/9 \cdot 0,059 \text{pH} - 1/9 \cdot 0,059 \lg[\text{CO}_3^{2-}]$		
2.7	$\text{PbS} + 4\text{H}_2\text{O} + \text{CO}_3^{2-} \rightleftharpoons \text{PbCO}_3 + \text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e}$	+40,03	+0,217
II.7	$E_7 = +0,217 + 1/8 \cdot 0,059 \lg[\text{SO}_3^{2-}] - 0,059 \text{pH} - 1/8 \cdot 0,059 \lg[\text{CO}_3^{2-}]$		
2.8	$3\text{PbS} + 14\text{H}_2\text{O} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Pb}_3(\text{OH})_2(\text{CO}_3)_2 + 3\text{SO}_4^{2-} + 26\text{H}^+ + 24\text{e}$	+149,9	+0,271
II.8	$E_8 = +0,271 + 1/8 \cdot 0,059 \lg[\text{SO}_3^{2-}] - 13/12 \cdot 0,059 \text{pH} - 1/12 \cdot 0,059 \lg[\text{CO}_3^{2-}]$		
2.9	$\text{PbS} + 2\text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_2 + \text{S}^0 + 2\text{H}^+ + 2\text{e}$	+34,9	+0,757
II.9	$E_9 = +0,757 - 0,059 \text{pH}$		
2.10	$2\text{PbS} + 7\text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_2 + \text{S}_2\text{O}_3^{2-} + 10\text{H}^+ + 8\text{e}$	+104,6	+0,567
II.10	$E_8 = +0,567 + 1/8 \cdot 0,059 \lg[\text{S}_2\text{O}_3^{2-}] - 5/4 \cdot 0,059 \text{pH}$		
2.11	$\text{PbS} + 6\text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_2 + \text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}$	+76,19	+0,413
II.11	$E_8 = +0,413 + 1/8 \cdot 0,059 \lg[\text{SO}_4^{2-}] - 5/4 \cdot 0,059 \text{pH}$		

$\text{PbCO}_3 \leftrightarrow \text{PbKx}_2$ , (pH from 7,0 to 9,5);

$\text{Pb}(\text{OH})_2(\text{CO}_3)_2 \leftrightarrow \text{PbKx}_2$ , (pH from 9,5 to 12);

$\text{Pb}(\text{OH})_2 \leftrightarrow \text{PbKx}_2$ , (by Mashevskii, pH from 7,0 to 12);

$\text{Kx}^- \leftrightarrow \text{Kx}_2$ ;

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  $\text{Me} - \text{X}$ . In result, the  $\text{X}^-$  ions become the potential determining ions. Thus the mineral surface potential will be described by the following equation:

$$E_1 = E_1^0 - \frac{0,059}{n} \cdot \lg(\text{X}^-);$$

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. So, quantitative values of xanthenes necessary concentration can be determined according to the equality  $E = E_1$ , allowing calculate  $(\text{X}^-) = f(\text{pH})$ . The further comparison of calculated and experimental results allows defining the xanthenes necessary concentration and factors influencing on its value.



Table 3. Addition

No react. and equat.	Reaction and equations	$\Delta F^0$ React. Kcal.	$E^0, V$
2.12	$PbS + 5H_2O \rightleftharpoons Pb(OH)_2 + SO_3^{2-} + 8H^+ + 6e$	+80,94	+0,585
II.12	$E_8 = +0,585 + 1/6.0,059\lg[SO_3^{2-}] - 4/3.0,059pH$		
2.13	$2X^- \rightleftharpoons X_2 + 2e$	- 4,61	- 0,100
II.13	$E_9 = -0,100 - 0,059.\lg[X] \quad [X_2] = 1,0$		
II.14	$E_{10} = -0,248 - 0,059.\lg[X] \quad [X_2] = 1.10^{-5}$		
II.15	$E_{11} = -0,203 - 0,059.\lg[X] \quad [X_2] = 3,18.10^{-4}$		
2.14	$PbS + 2X^- \rightleftharpoons PbX_2 + S^0 + 2e$	-9,38	-0,203
II.16	$E_{14} = -0,203 - 0,059\lg[X]$		
2.15	$2PbS + 4X^- + 3H_2O \rightleftharpoons 2PbX_2 + S_2O_3^{2-} + 6H^+ + 8e$	+24,11	+0,131
II.17	$E_{15} = +0,131 + 1/8.0,059\lg[S_2O_3^{2-}] - 3/4.0,059pH - 1/2.0,059\lg[X]$		
2.16	$PbS + 2X^- + 3H_2O \rightleftharpoons PbX_2 + SO_3^{2-} + 6H^+ + 6e$	+44,59	+0,322
II.18	$E_{16} = +0,322 + 1/6.0,059\lg[SO_3^{2-}] - 0,059pH - 1/3.0,059\lg[X]$		
2.17	$PbS + 2X^- + 4H_2O \rightleftharpoons PbX_2 + SO_4^{2-} + 8H^+ + 8e$	+40,04	+0,217
II.19	$E_{17} = +0,217 + 1/8.0,059\lg[SO_4^{2-}] - 0,059pH - 1/4.0,059\lg[X]$		

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.

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 ( $PbS \leftrightarrow Pb(OH)_2$  and  $PbS \leftrightarrow PbX_2$ ), and also ( $PbS \leftrightarrow Pb(OH)_2$  and  $X^- \leftrightarrow X_2$ ) are impossible, because calculation results do not coincide with experimental data (figure. 4.a and 5.d).

It contradicts Mashevskii's results. Besides lead hydroxide in open system couldn't be formed, as at any pH values they supersede in lead carbonates.

However, calculations results at equilibrium conditions  $PbS \leftrightarrow PbCO_3$ ;  $Pb_3(OH)_2(CO_3)_2$  and  $X^- \leftrightarrow X_2$  coincide experimental results only in case of elementary sulfur ( $S^0$ ) formation at dixanthenes concentration equal  $3,18.10^{-4}$  mol/l, assuring the formation of lead xanthenes on mineral surface with elementary sulfur sharing out (see figure 4.b), and similar results at equilibrium condition  $PbS \leftrightarrow PbCO_3$ ;  $Pb_3(OH)_2(CO_3)_2$  and  $PbS \leftrightarrow PbX_2$ . (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  $PbCO_3$ , pH from 7,0 up to 9,0:

$$\lg [X]_{neces.} = -2,98 + \frac{1}{2}.\lg[CO_3^{2-}]; \dots\dots\dots (3)$$

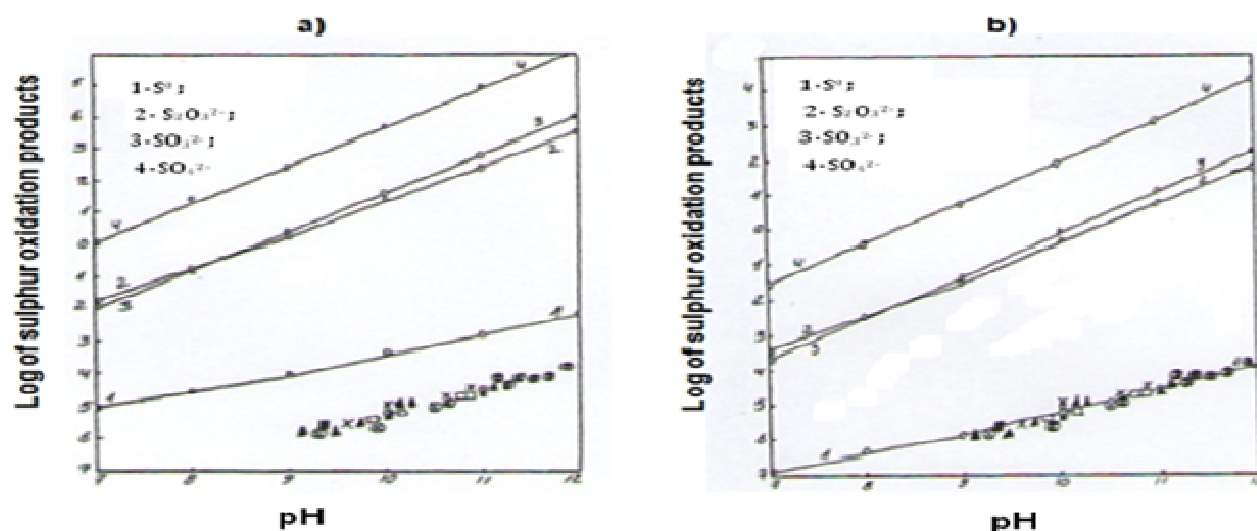
b/ in condition of lead hydro carbonate formation  $Pb_3(OH)_2(CO_3)_2$ , pH from 9,0 up to 12:

$$\lg [X]_{nec.} = -6.66 + 1/3.pH + \frac{1}{2}.\lg[CO_3^{2-}]; \quad (4)$$

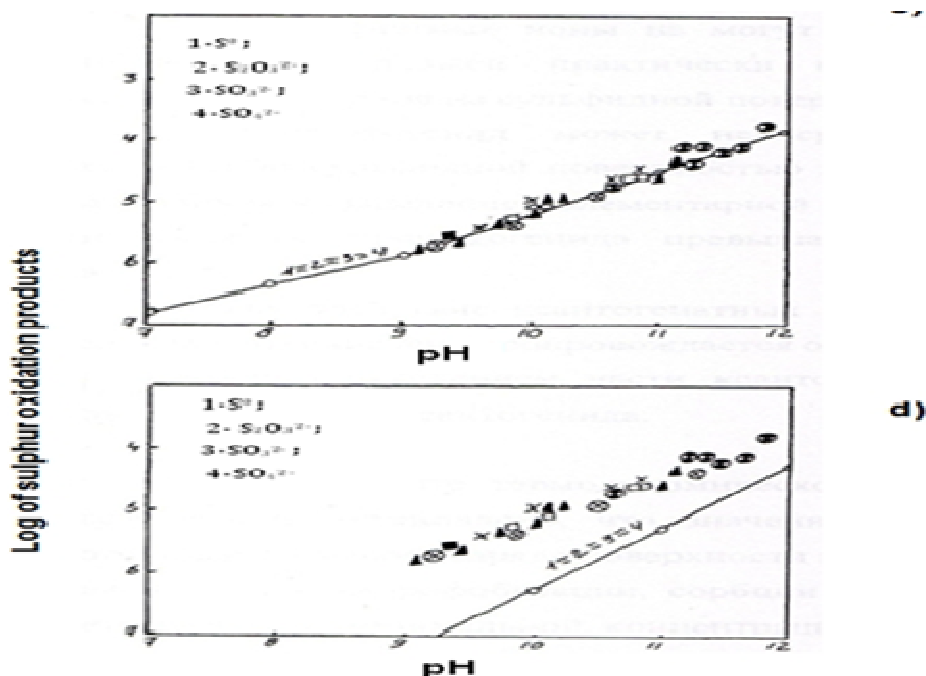
These last dependences represent quantitative physico-chemical models of lead sulfide flotation process. The elaborated models (3) and (4) can be used as a task of functional block in automation system of control and regulation flotation process in the plants.

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:  $1,2.10^{-7}$  at pH –7;  $4,0.10^{-7}$  at pH – 8;  $1,2.10^{-6}$  at pH – 9;  $8,5.10^{-6}$  at pH – 10;  $2,9.10^{-5}$  at pH – 11;  $1,3.10^{-4}$  at pH – 12.





**Figure 4.** Influence of pH on butyl xanthenes necessary concentration in galena flotation:  $[X_2] = 10^{-5}$  (a);  $3,18 \cdot 10^{-4}$  (b). In equilibrium conditions of:  $PbS \leftrightarrow PbCO_3$ ;  $Pb_3(OH)_2(CO_3)_2$  and  $X^- \leftrightarrow X_2$ . (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 AA, 1978)).



**Figure 5.** Influence of pH on butyl xanthenes necessary concentration in galena flotation in equilibrium conditions of:  $PbS \leftrightarrow PbCO_3$ ;  $Pb_3(OH)_2(CO_3)_2$  and  $PbS \leftrightarrow PbX_2$  (C);  $PbS \leftrightarrow Pb(OH)_2$  and  $PbS \leftrightarrow PbX_2$  (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], (Abramov AA, 1978)).

## 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.
- pH 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 pH value corresponding to minimum charge potential of lead xanthenes surface, presents the most important condition of maximum hydrophobicity, dexanthenes sorption and mineral floatability at minimum collector concentration in solution. The given pH 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.

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