



ISSN: 0975-833X

RESEARCH ARTICLE

SPHALERITE AND ITS DEPRESSION OPTIMAL CONDITIONS BY ZINC SULPHATE

¹Chettibi, M., ¹Boutrid, A. and ²Abramov, A. A.

¹"Badji Mokhtar" Annaba University, BP. 12, Annaba, Algeria

²Moscow State Mining University, Leninskii pr. 6, 117049 Moscow, Russia

ARTICLE INFO

Article History:

Received 18th November, 2013

Received in revised form

10th December, 2013

Accepted 15th January, 2014

Published online 28th February, 2014

Key words:

Physicochemical Modeling,
Flotation, Depression, Minerals interaction,
Sphalerite, Zinc sulphate.

ABSTRACT

As a result of theoretical and experimental investigations it has been shown, that for preventing sphalerite activation by copper and lead ions, it is required to create practically the same concentration value of sulphur ions, which abruptly increases by raising the pH value of pulp liquid phase. Physico-chemical model derived can be used as the criteria for functional units of automation systems to control and regulate sulphuric sodium expenses. The depression selectivity action of zinc sulphate on sphalerite depends on the solubility and the maximal stability of hydroxide zinc dregs in pulp and on sphalerite surface. According to those conditions, consequently, a hydrophobic interaction is carried out between dregs and mineral oxidation product where the potential value of both products is near zero, and the crystalline corresponding characteristics of zinc salts and minerals.

Copyright © 2014 Chettibi, et al. 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). Properties of zinc sulfides flotation are generally determined by mineral crystal structure, both electronic defective characteristics and changes in them at the admixture structure variation. During crushing and flotation, poly-metallic ores may inter-activate each other; it means mineral cationic sorption on surface of others (Gaudin *et al.*, 1959; Avdokhin and Abramov 1989). "Natural" activation can change essentially flotation properties of a mineral and efficiency of their division. Therefore the analysis of sphalerite and zinc sulfides surface state, inter-action conditions of sulfuric minerals and its prevention represent theoretical and practical interest (Chettibi 2002; Plaksin 1960). By results of theoretical researches and their comparisons to experimental data it is established, that the obtained equations of the necessary concentration of sulfur ions for preventing sphalerite activation by lead and copper ions, are models which can be used as task to the automatic system control of the sulfuric sodium charge in corresponding cycles of selective flotation (Abramov 1978; Melik-Gaykazian and Abramov 1990). In the present paper, by using method of thermodynamic analysis, it was defined the zinc sulfides and sphalerite surface state, the interaction conditions of sulfide minerals, the prevention of sphalerite activation by lead and

copper ions, the establishment of new physicochemical models and the optimum conditions of sphalerite depression by zinc sulfate ions.

MATERIALS AND METHODS

The main method used in this work for computing, characterizing and modeling Sphalerite depression by zinc sulfate 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; Abramov 1993). This method allowed us to define the composition of the salts liaisons, representing the minerals surfaces, to carry out physico-chemical 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 1978):

- 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:

*Corresponding author: Chettibi, M.

"Badji Mokhtar" Annaba University, BP. 12, Annaba, Algeria.

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

$$\text{Or at } 25^\circ \text{C } \Delta F_r^0 = -1,364.\lg K$$

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

$$\Delta F_r^0 = -n.F.E^0 \quad (2.3)$$

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

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

Or at temperature 25°

$$E = E^0 + \frac{0,059}{n} \log \frac{[C]^c.[D]^d}{[A]^a.[B]^b}$$

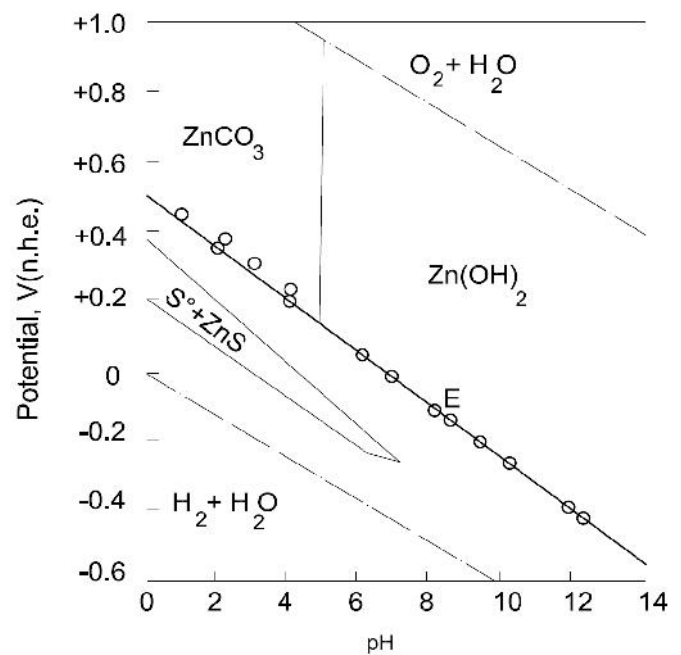
It was confirmed theoretically and experimentally in different works (Abramov 1977; Abramov 1978; Abramov 1993; Forssberg *et al.*, 1984) the possibility of estimating the surface quality of minerals salt, based on thermodynamic calculation. The point of this method is to create system of basic reactions 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 investigating the standard free energies of formation (in Kcal/mol) of species and compounds were used (in Kcal/mol) After Latimer *et al.* (1952) PbS -22,15; PbCO₃ -149,7; Pb₃(OH)₂(CO₃)₂ -406,0; Pb²⁺ -5,81; S²⁻ +22,1; H₂S -6,54; SO₃²⁻ -116,10; SO₄²⁻ -177,34; CO₃²⁻ -126,22; HCO₃⁻ -140,31; OH⁻ -37,595; H₂O -56,69; Zn(OH)₂ -132,60; Zn²⁺ -35,184; ZnO₂²⁻ -93,03; CuS -11,7. After Garrels and Christ (1964) S₂O₃²⁻ -127,20; ZnCO₃ -174,8; HZnO₂⁻ -110,9; Zn(OH)⁺ -78,70; Cu₂(OH)₂CO₃ -216,44; Cu(OH)₂ -85,3; Cu⁺ +15,53; Cu²⁺ +12,0. After Karpov *et al.* (1958) ZnS -47,4. Experimental results were collected from different bibliographies. They were compared with the computed ones in order to validate them and to prove their reliability.

RESULTS AND DISCUSSIONS

Valuation of zinc sulfide surface state

For an estimation of zinc sulfide and sphalerite surface state, as possible products of zinc sulfides oxidations were considered: ZnS, Zn(OH)₂, ZnCO₃, Zn²⁺, HZnO₂⁻, ZnO₂²⁻, Zn(OH)⁺, SO₄²⁻, SO₃²⁻, S₂O₃²⁻. In calculations were used reactions (1.1) - (1.8) (table 01); thus obtained on the basis of reactions (1.1) - (1.2) and equations (I.1) - (I.2) (see table 01) are the computing equations of inter - phase transitions potential: sulfide of zinc - the oxidized combinations of zinc. The equations (I.3) - (I.4), obtained on the basis of reactions (1.3) - (1.4) also, used for estimation of stability borders of zinc sulfide. In order to

estimate the oxidation products stability, we used the equations (I.5) and (I.6), obtained on the basis of balance constant expression of reaction (1.5), the equations (I.11), and the equations (I.7), which were obtained on using the reaction (1.6). The pH value of ZnCO₃ and Zn(OH)₂ transition in the condition of caustic sodium, has been found from the equation (I.9), obtained by settling the system of equations obtained from the expressions of constant balance reactions (1.10), (1.11), (1.12), (1.5) - (1.8) and the equation (I.4). While computing, the total activity of carbonic combinations in solution was taken equal 10⁻⁵ mol/l, and sulfuric 10⁻⁴ mol/l, (Abramov 1978). The obtained results agree with results of Abramov's work (Abramov 1978). These earlier results has been illustrated in figure 01, They testify that the primary product of sphalerite oxidation up to 5,17 is the zinc carbonate, and at higher values - zinc hydroxide.



Note:

- O₂ + H₂O : higher limit of water stability
- H₂ + H₂O : lower limit of water stability

Figure 1. Influence of pH and solution Redox potential on the sphalerite surface state

Analysis of sulfuric minerals interaction possibility and conditions of its prevention

The analysis of sulfuric minerals activation possibility by copper and lead ions, which are supplied at the solution by oxidation products, corresponding sulfuric minerals in the presence of the dissolved air carbonic acid ($C = 10^{-5}$ mol/l) and the concentration of sulfate ions equal 10⁻³ mol/l took into account, that products of galena oxidation in these conditions up to 9 are lead carbonate and copper hydro-carbonate, and at from 9 up to 12-accordingly lead hydro-carbonate and hydroxide bivalent copper (Abramov *et al.*, 1982; Chettibi 2002). Product of sphalerite oxidation in neutral and alkaline surroundings is Zn(OH)₂ (see Figure 01). Solubility product of these combinations, obviously, also will supervise

Zn²⁺ concentration and concentration of "activating" ions of b²⁺ and u²⁺ in pulp liquid phase.

Table 1. The thermodynamic characteristics (F⁰, E⁰) reactions and equations

N ^o equation & reactions.	reactions & equations	F ⁰ reactions, Kcal.	E ⁰ , V
1.1	2ZnS + 3H ₂ O + 2CO ₃ ²⁻ = 2ZnCO ₃ + S ₂ O ₃ ²⁻ + 6H ⁺ + 6e	+40,510	+0,214
1.1	E = +0,214 - 3/4.0,059.pH - 1/4.0,059.log(CO ₃ ²⁻) + 1/8.0,059.log(S ₂ O ₃ ²⁻)		
1.2	2ZnS + 7H ₂ O = 2Zn(OH) ₂ + S ₂ O ₃ ²⁻ + 10H ⁺ + 8e	+97,17	+0,526
1.2	E = +0,526 - 5/4.0,059.pH + 1/8.0,059.log(S ₂ O ₃ ²⁻)		
1.3	2ZnS + 3H ₂ O = 2Zn ²⁺ + S ₂ O ₃ ²⁻ + 6H ⁺ + 8e	+67,302	+0,364
1.3	E = +0,364 - 3/4.0,059.pH + 1/4.0,059.log(Zn ²⁺) + 1/8.0,059.log(S ₂ O ₃ ²⁻)		
1.4	2ZnS + 7H ₂ O = 2HZnO ₂ + S ₂ O ₃ ²⁻ + 12H ⁺ + 8e	+142,63	+0,773
1.4	E = +0,773 - 3/2.0,059.pH + 1/4.0,059.log(HZnO ₂) + 1/8.0,059.log(S ₂ O ₃ ²⁻)		
1.5	ZnCO ₃ = Zn ²⁺ + CO ₃ ²⁻	+13,396	
1.5	logK ₅ = log(Zn ²⁺) + log(CO ₃ ²⁻) = log(Zn ²⁺) + log{CK ₁₁ K ₁₂ / (K ₁₁ K ₁₂ + K ₁₂ (H ⁺) + (H ⁺) ²)}		
1.6	logK ₅ = log(Zn ²⁺) + log(CO ₃ ²⁻) = log(Zn ²⁺) + log{K ₁₁ K ₁₂ (K _w + 2C(H ⁺) - (H ⁺) ²) / (K ₁₂ + 2(H ⁺))}		
1.6	Zn(OH) ₂ = H ⁺ + HZnO ₂ ⁻	+22,730	
1.7	Log K ₆ = log(HZnO ₂ ⁻) - pH		
1.7	Zn(OH) ₂ = Zn ²⁺ + 2OH ⁻	+23,256	
1.8	Zn(OH) ⁺ = Zn ²⁺ + OH ⁻	+5,921	
1.9	HZnO ₂ ⁻ = ZnO ₂ ²⁻ + H ⁺	+17,87	
1.10	H ₂ O = H ⁺ + OH ⁻	+19,60	
1.11	HCO ₃ ⁻ = H ⁺ + CO ₃ ²⁻	+14,09	
1.12	H ₂ CO ₃ = H ⁺ + HCO ₃ ⁻	+8,69	
1.8	Na ⁺ + 2Zn ²⁺ + Zn(OH) ⁺ + H ⁺ = 2CO ₃ ²⁻ + HCO ₃ ⁻ + OH ⁻ + HZnO ₂ ⁻ + 2ZnO ₂ ²⁻		
1.9	(CK ₁₁ K ₁₂ K ₇ - K ₅ K _w)(H ⁺) ² + K ₁₂ K ₅ K _w ² (H ⁺) - K ₁₁ K ₁₂ K ₅ K _w ² = 0		
1.10	2K ₁₁ K ₁₂ K ₇ ² K ₈ (H ⁺) ³ + K ₁₁ K ₁₂ K ₇ ² K _w (H ⁺) ² + 2K ₈ K _w ² (K ₅ K _w ² - CK ₁₁ K ₁₂ K ₇)(H ⁺) + K ₁₂ K ₈ K _w ² (K ₅ K _w ² - K ₁₁ K ₇ K _w - K ₁₁ K ₆ K ₇ - 2K ₁₁ K ₇ K ₉) = 0		
1.11	(CO ₃ ²⁻) = CK ₁₁ K ₁₂ / (K ₁₁ K ₁₂ + K ₁₂ (H ⁺) + (H ⁺) ²);		

Thus, concentration of b²⁺ ions can be calculated (Table. 2) on the basis of reactions (1.13) and (1.14) including the expression (1.11), and the equations (I.16) (up to 9) and (I.17) (at 9-12), and concentration of ions u²⁺ - on the basis of reactions (1.15 - 1.16) and the equations (I.19) (<9) and (I.20) (> 9). Calculations results of available and necessary ratio copper and lead ions concentration for sphalerite activation at various values are represented on figure 02. They show that in considered conditions, presence of copper minerals should cause strong sphalerite activation (curve ZnS and u²⁺) and that, was proved in practice (Bogdanov *et al.*, 1959; Mitrofanov 1967). Also, presence of

galena in the pulp can cause sphalerite activation (curve ZnS + b²⁺), the received laws of sulfuric minerals inter-activation in considered conditions will not be changed, if the source of b²⁺ and u²⁺ ions in liquid phase of pulp is not minerals and their oxidation products, but specially encumbered lead and copper salts. Minimally necessary (S²⁻) preventing sphalerite activation by u²⁺ ions, can be computed by using in the equation (I.22), received on the bases of reaction (1.24), instead of lg (u²⁺) the values of the right parts of the equation (I.14), after substitution in them log (Zn²⁺) expressions from the equation (I.18). Similarly the necessary S²⁻ ions concentrations for prevention of sphalerite activation by b²⁺ ions can be found, using in the equation (I.24), obtained on the basis of reactions (1.25), instead of log (b²⁺) the right part value of the equation (1.20), after substituting in it the expressions for log (Zn²⁺) from the equation (I.18) (see Table 2). Results of the carried out calculations show, that prevention of sphalerite activation by u²⁺ and b²⁺ ions demands creation in the liquid phase of a pulp practically the same (S²⁻) which sharply grows increasing values (figure.03). In conditions of the lead flotation spent usually at about 8, necessary for prevention of zinc sulfides activation by copper ions the concentration (S²⁻), according to the equation (I.25), should make:

$$\log(S^{2-}) = -36,8 + 2,8 = -20,8; \text{ or } (S^{2-})_{\text{critic}} = 10^{-20,8} \text{ mol/l.}$$

At measurement of sulfuric ions concentration by silver sulfide electrode, potential Es which in relation to a normal hydrogen electrode is defined by the equation:

$$E_s = -0,713 - 0,0295 \log(S^{2-}),$$

electrode potential value:

$$E_s = -0,713 - 0,0295 * (-20,8) = -0,101 \text{ V.}$$

Hence, supporting concentration of sulfide ions in a limit 10⁻¹⁹ - 10^{-20,8} mol/l (8), it is possible to provide prevention of sphalerite activation and successful lead minerals flotation. This was proved in the researches results earlier obtained in the cycle of lead-copper flotation on Zaryanovskaya factory (Abramov 1983).

Depression of zinc sulfides by zinc sulfate in cycle of lead flotation

Sphalerite depression with insignificant contents of copper impurity is carried out only by encumbering the zinc sulfate. Depression action of zinc sulfate on sphalerite is related to the presence of zinc containing colloidal haste on its surface. Such haste is formed in pulp as a result of the encumbered zinc sulfate with the dissolved air carbonic acid interaction and contains in its structure hydroxide and carbonate ions. In neutral and alkaline surroundings, zinc containing haste sticks to the surface of all sulfide minerals (galena, pyrite and sphalerite), but strong depression action renders only on sphalerite. The depression action selectivity of zinc sulfate on sphalerite surface is caused by the same cation in haste that improves haste fastening on mineral surface and contributes to the formation of more dense and stronger schlamms covering on zinc sulfides in comparison with other sulfides.

Table 2. The thermodynamic characteristics (F⁰, E⁰) reactions and equations

react.& equat.	reactions and equations	Log K	F ⁰ reaction Kcal.	used react. & equat.
I.13	$PbCO_3 \rightleftharpoons Pb^{2+} + CO_3^{2-}$	$K_{20}=1,11^* \cdot 10^{-13}$	+17,67	
I.14	$H_2S + 4H_2O \rightleftharpoons SO_4^{2-} + 10H^+ + 8e$		+55,94	
I.15	$Cu_2(OH)_2CO_3 + 2H^+ \rightleftharpoons 2Cu^{2+} + 2H_2O + CO_3^{2-}$		+7,60	
I.16	$Cu(OH)_2 + 2H^+ \rightleftharpoons Cu^{2+} + 2H_2O$		-12,55	
I.17	$2ZnS_{sph.} + 7 H_2O \rightleftharpoons 2 Zn(OH)_2 + S_2O_3^{2-} + 10H^+ + 8e$		+97,17	
I.12	$Log(Cu^{2+}) = -2,78 - pH - 1/2log(CO_3^{2-})$			I.15
I.13	$Log(Cu^{2+}) = +9,2 - 2pH$		-12,55	
I.18	$ZnS + Cu^{2+} \rightleftharpoons CuS + Zn^{2+}$	+10,95	-5,01	
I.14	$Log(Cu^{2+}) = -11,00 + log(Zn^{2+})$			I.18
I.19	$ZnS + Pb^{2+} \rightleftharpoons PbS + Zn^{2+}$	+3,02	-4,12	
I.20	$Log(Pb^{2+}) = -3,02 + log(Zn^{2+})$			I.19
I.15	$Log(Cu^{2+}) = -7,98 + Log(Pb^{2+})$			
I.16	$log(Pb^{2+}) = -12,82 - log\left(\frac{K_{12} \cdot 11}{11 \cdot 12^+ \cdot 12[H^+] + [H^+]^2}\right)$			
I.21	$Pb_3(OH)_2(CO_3)_2 + 2H^+ \rightleftharpoons 3 Pb^{2+} + 2CO_3^{2-} + 2H_2O$	-16,67	+22,75	
I.17	$log(Pb^{2+}) = -5,56 - 2/3 pH - 2/3log\left(\frac{12 \cdot 11}{11 \cdot 12^+ \cdot 12[H^+] + [H^+]^2}\right)$			
I.22	$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2H_2O$	+11,70	-15,96	
I.18	$lg(Zn^{2+}) = +11,70 - 2 pH$			I.22
I.19	$log(Cu^{2+}) = -2,78 - pH - 1/2log\left(\frac{12 \cdot 11}{11 \cdot 12^+ \cdot 12[H^+] + [H^+]^2}\right)$			I.15, I.12,
I.23	$Cu^+ \rightleftharpoons Cu^{2+} + 2e$		+ 3,53	
I.20	$E = 0,153 + 0,059 log(Cu^{2+}) - 0,059 Log(Cu^+)$			I.23
I.21	$log(Cu^{2+}) = +1,65 + log(Cu^+) - 5/4pH$			I.22, I.23
I.24	$CuS \rightleftharpoons Cu^{2+} + S^{2-}$	-36,10	+49,33	
I.22	$E = +0,526 - 5/4 \cdot 0,059 \cdot pH + 1/8 \cdot 0,059 log(S_2O_3^{2-})$			
I.23	$log(S^{2-}) = -36,10 - log(Cu^{2+})$			I.24
I.25	$PbS \rightleftharpoons Pb^{2+} + S^{2-}$	-28,15	+38,44	
I.24	$log(S^{2-}) = -28,15 - log(Pb^{2+})$			I.25
				I.14, I.18, I.23
I.25	$log(S^{2-}) = -36,10 - log(Cu^{2+}) = -36,80 + 2pH$			
I.26	$log(S^{2-}) = -28,15 - log(Pb^{2+}) = -36,83 + 2pH$			I.20, I.18, I.24

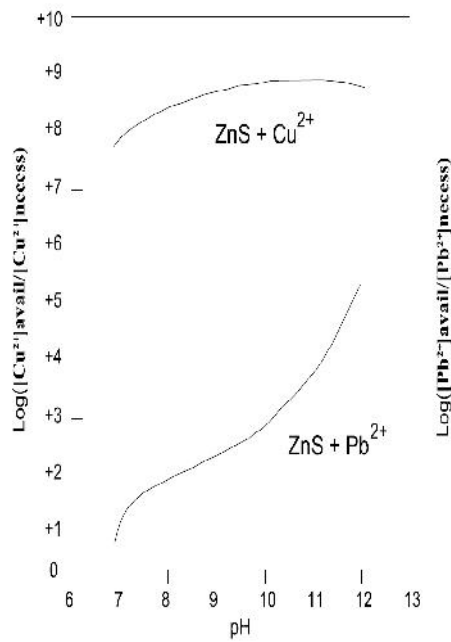


Figure 2. Influence of pH on the available in solution and necessary for sphalerite activation concentrations ratio of copper and lead ions in pulp liquid phase

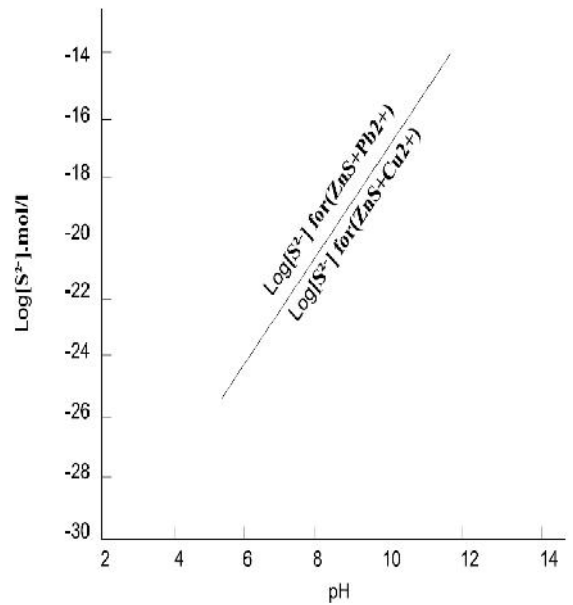


Figure 3. Influence of pH on ions sulfides concentration values (S²⁻), necessary for preventing sulfide minerals interaction

The greatest haste depression ability is observed at the moment of their formation when crystal trellis was not generated yet and unsaturated haste valence connections are compensated by the unsaturated connections of sphalerite surface. The crystal haste, for example $Zn(OH)_2$, received at additional encumbering caustic sodium in pulp (<11), is not able to depress the sphalerite flotation. In the acid surroundings sulfate zinc also cannot be a depressor for sphalerite because in these conditions the haste is not formed. Results of the carried out calculations in view of reaction (1.26) - (1.30) and balance constant expressions (I.27) - (I.31), (see table 03) show, that the minimal solubility and the maximal stability of zinc hydroxide haste in pulp and on the sphalerite surface are observed at pH values (8,6 - 9,5) (figure 04), replying to pH value of surface minimal charge, both of sphalerite oxidation products and $Zn(OH)_2$ haste providing the best results of sphalerite depression by zinc sulfate and the maximal flotation selectivity (Abramov 1983). The connection stability of haste with mineral surface, as well as selectivity of its sticking, are defined by interaction both of haste and mineral oxidation products at potential close to zero charge potential, number of mutually compensated connections at fastening and the crystal lattices parameters conformity of haste and mineral. In all cases, however, its stability is smaller than xanthate chemical sorption connection; therefore haste fastening proceeds without replacement of the collector from mineral surface.

According to other concrete material structure particularities of processed raw material, we can use the admixtures of sulfate zinc with various reagents (caustic sodium, soda, etc.). For example, the sulfate zinc and soda admixture can be used for eliminating iron and copper from the draft zinc concentrates. Grosman L.I. and Khadzhiev P.G. showed that amorphous haste of the basic zinc carbonate with particles size from the tenth shares of micron up to several microns can be formed in conditions of sphalerite depression by sulfate zinc in the soda surrounding. Efficacy of sphalerite depression by such haste decreases first by increasing pulp temperature, than at pulp values more than 10,5, later by adding liquid glass and bringing in copper ions in pulp, finally by increasing either the duration and intensity of hashing or the collector dosage, it means in all cases, causing the stability feebleness of haste connection or removal from mineral surface. In optimal conditions the sulfate zinc dosage makes usually (2 - 4) kg/t and soda (01) kg/t of draft zinc concentrate.

Table 3. The thermodynamic characteristics (F^0, E^0) reactions and equations

react. & equa	reactions and equations	logK	F0 * 4,184j.
I.26	$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH^-$	-17,05	+23,26
I.27	$K_1 = (Zn^{2+}) (OH^-)^2$		
I.27	$Zn(OH)^+ \rightleftharpoons Zn^{2+} + OH^-$	-4,34	+5,92
I.28	$K_2 = (Zn^{2+}) (OH^-) / (Zn(OH)^+)$		
I.28	$Zn(OH)_2 \rightleftharpoons H^+ + HZnO_2^-$	-16,65	+22,73
I.29	$K_3 = (H^+) (HZnO_2^-)$		
I.29	$HZnO_2^- \rightleftharpoons H^+ + ZnO_2^{2-}$	-13,10	+17,87
I.30	$K_4 = (H^+) (ZnO_2^{2-}) / (HZnO_2^-)$		
I.30	$H_2O \rightleftharpoons H^+ + OH^-$	-14,00	+19,10
I.31	$K_w = (H^+) (OH^-)$		

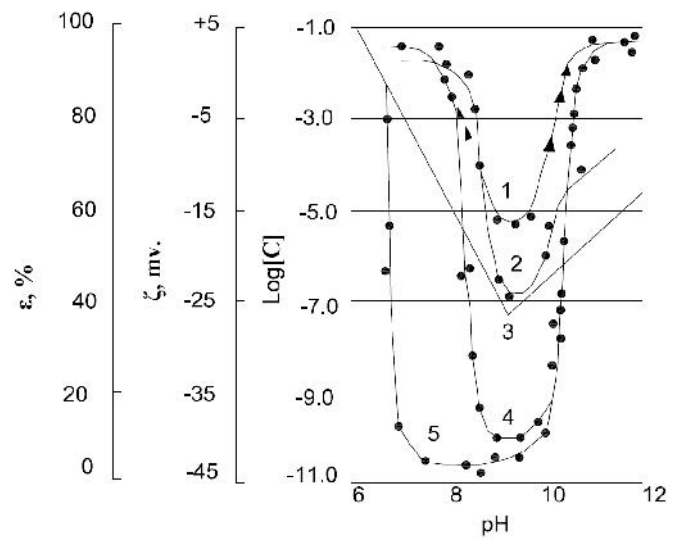


Figure 04. pH influence on log(C), total ions value concentration Zn^{2+} , $Zn(OH)^+$, $HZnO_2^-$ and ZnO_2^{2-} in the solution (3) at the zinc hydroxide haste presence; its electro-kinetic potential (2); floatability of naturally activated sphalerite in sodium caustic surroundings without depressor (1), with zinc sulfate (1,33 g/l), in sodium caustic surroundings (4) and in soda surroundings (5) at initial concentration of butyl xanthate 12 mg / l (according to P.G. Khadzhiev and L.I. Grosman(Abramov 1983)).

The copper elimination technology of zinc concentrates, consists in preliminary bringing out the collector from minerals surface by sulfuric sodium and flotation of copper sulfides with zinc sulfides depression by zinc hydrate at $= 6,0 \div 6,7$. As result of copper elimination, it was possible to increase the zinc content in the concentrate from 46 till 54 %, with simultaneous decrease of the copper content in it from 4,44 till 1,57 %. Thus, the zinc extraction can reach up to 89 % from initial concentrate. The general extraction of copper from ores grew by (2 ÷ 3) %. The positive effect of draft zinc or collective concentrate ultimate grinding is defined, first, by not only the decreasing of (S^{2-}) ions, but also the peeling of sphalerite activating pellicles, which help its depression. Second, the collector surplus in liquid phase of pulp is absorbed by the fresh reformed sulfides surface and consequently we observed redistributions of the collector and reduction of its concentration in pulp. At last, in the ultimate grinding process we found additional disclosing sphalerite joints to other sulfides and that causes deterioration of copper-iron product quality.

Conclusion

According to thermodynamic calculations and experimental results we can conclude the following:

- Presence of copper minerals should cause strong sphalerite activation, somewhat improves the pyrite floatability and do not present any influence on galena flotation property. Presence of galena in pulp can cause only sphalerite activation.
- Prevention of sphalerite activation by Cu^{2+} and Pb^{2+} ions demands creation in the liquid phase of pulp practically the same (S^{2-}) which sharply grows increasing values. The

obtained equations (I.25) and (I.26), necessary concentration of S^{2-} ions preventing sphalerite activation by b^{2+} and u^{2+} ions, can be used as the task to automatic control system of the sulfuric sodium charge in corresponding cycles of selective flotation.

- Selectivity of zinc sulphate depression actions on sphalerite at $pH = 8,6 \div 9,5$ is caused by the solubility and the maximal stability of zinc hydroxide haste in pulp and on sphalerite surface, in these conditions owing to interaction of haste and mineral oxidation product at potential close to zero and parameters conformity of both haste and mineral crystal lattices. The best results of sphalerite depression by zinc sulphate and the maximal selectivity of flotation is reached in this area of values 8,6 - 9,4.

REFERENCES

- Abramov A. A. 1977. Physicochemical modelling of flotation systems, Moscow, ed. "MISIS", Russia.
- Abramov A. A., 1978, Theoretical principles of optimizing sulfide ores selective flotation. Moscow. "Nedra". 1978.
- Abramov A. A., 1983, Flotation technology of processing bloom minerals. Moscow, "Nedra", 1983.
- 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".
- Avdokhin V. M., Abramov A. A. 1989, Minerals sulfide oxidation in flotation process. Moscow, Nedra edition.
- Bogdanov O. S., Podnec A. K., Khainman V. Y. *et al.* 1959, Query of theory and flotation technology. Works of VNIPI Mekhanobr, Journal N^o 124, 1959.
- Chettibi M., 2002, "Optimisation of sulphide minerals (PbS, ZnS and FeS) flotation", PhD Thesis, Moscow State Mining University, Mineral Processing Department, July 2002.
- 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.
- Garrels R. M., Christ C. L., 1964. Solutions, Minerals and Equilibria. Freeman, San Francisco, California, USA.
- Gaudin A. M., Fuerstenau D. W., *et al.*, 1959, Activation and deactivation studies with copper on sphalerite. Min. eng., V. 1, N 4, 1959,
- Karpov J. K., Kashik S. A., and Pampura V. D., 1958. Constants of substances for thermodynamic calculations in geochemistry and petrography. Moscow, ed. "Nedra", p 142, Russia.
- Latimer W. M., 1952. Oxidation potentials. New York, Prentice and Hall, 2nd edition.
- Melik-Gaykazian V. I., Abramov A. A., 1990. Investigation methods of flotation process. Moscow, Nedra.
- Mitrofanov S. I., 1967, Selective flotation. Moscow, "Nedra", 1967.
- Plaksin I. N., 1960. Evolution of mineral processing theory and technique. CIIN CM, N^o1.
- Wills B. A., 2005. Mineral Processing Technology. London, Elsevier edition, V.7.
