

*Full Length Research Paper*

# Modelling of pyrite depression process by lime in copper and zinc flotation

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**As the result of theoretical and experimental investigations in laboratory and industrial scale physico-chemical models for optimal conditions of copper, zinc and iron sulphides flotation and depression have been derived, verified and proved. Physico-chemical models derived are based on the mechanism of reagents action and represent themselves determined quantitative relationships between concentrations of reagents ions in pulp. They can be used at plants, firstly, for examination and imperfection of technological processes of copper or zinc flotation at depression of iron sulphides by lime and, secondly, as the criteria for functional units of automation systems in optimization of these process.**

**Keywords:** Flotation, Depression, Thermodynamic models, Pyrite, Zinc, Copper, Lime, Xanthenes.

## INTRODUCTION

Flotation of copper or zinc sulphides by depression of the iron sulphides in selective flotation or in separation of bulk copper-pyrite or zinc-pyrite concentrates is realized as usual in alkaline environment created by lime (Abramov, 1983). However, the maximum recovery of copper or zinc into concentrates of high quality especially from complexe ores is always troublesome task (Abramov, 1983; Arslan et al., 1998; Sirkeci et al., 1999; Terblanche et al., 1998).

Previous investigations (Abramov, 1978) have shown that the quantitative relationships between the necessary concentrations of reagents in pulp for the optimal conditions of technological processes can be derived by thermodynamic analysis of possible reactions of collector in the vicinity of minerals surface by comparing the results obtained with experimental data. The thermodynamic analysis methodology and deriving of the quantitative relationships between the necessary concentrations of reagents in pulp at boundary conditions of mineral flotation described in detail by Abramov (1978). Such models can be used: Firstly, for the analysis and improvement of selective flotation processes and,

secondly, as the criteria for functional units of automation control systems for regulation at the concentration plants.

The present paper describes the results of investigations and elaboration of models for iron sulphides depression (pyrite, pyrrhotite) by lime in copper or zinc flotation.

## RESULTS AND DISCUSSION

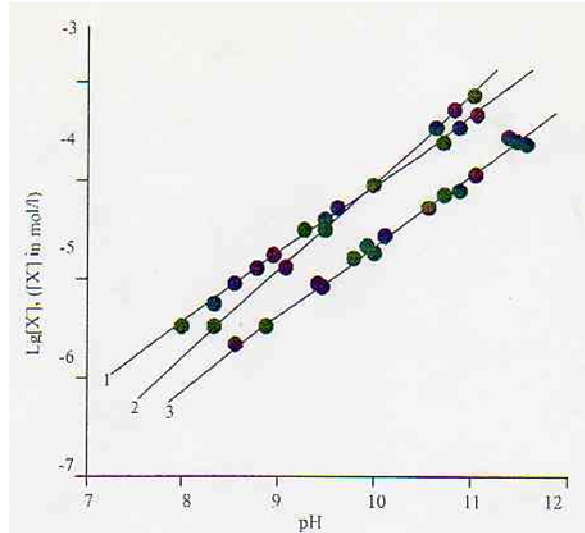
### Optimal conditions of iron, copper and zinc sulphides flotation

For determination of minimum-required concentration of xanthate ions  $[X^-]$  in pulp for maximum flotation of minerals at different pH values, the samples of pyrite of Zirianovskoye, Akchatausskoye and Belousovskoye deposits, pyrrhotite of Norilskoe and Zhdanouskoe deposits and chalcopyrite of Zirianovskoye and Belousovskoye deposits have been used. Results of their flotation have shown that it depends sharply on pH values (Figure 1) and does not depend on the genesis of minerals. Mineral samples taken from different deposits require for their complete (maximum) recovery the similar  $[X^-]$  at any pH value.

Relationships between xanthate  $X^-$  and hydrogen  $H^+$  ions concentrations  $[X^-] = f(pH)$  ensuring maximum

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**Figure 1.** Effect of pH value on the required concentration (mol/l) of ethyl xanthate [X] ensuring maximum pyrite (1), Pyrrhotite (2) and chalcopyrite (3) flotation.

Floatability of copper and iron sulphides in the absence of lime can be explained by taking into account the composition of natural sulphides oxidation products (Abramov 1978). Early, it has been found that for iron sulphides it will be ferric hydroxide and for chalcopyrite the mixture of cupric hydro-carbonate (pH < 9) or cupric hydroxide (pH > 9) with ferric hydroxide (Abramov 1978).

Results of thermodynamic analysis and their comparison with experimental data (fig. 1) has shown that the experimental relationship  $[X] = f(\text{pH})$  obtained for pyrite and pyrrhotite (fig. 1) can be explained by assuming that the necessary [X] value is determined by the  $[\text{FeOH}^+]$  value in the vicinity of the surface during the conversion of  $\text{FeS}_2$  and  $\text{FeS}$  to  $\text{Fe}(\text{OH})_3$  (the basic product of iron sulphides oxidation) (Abramov and Avdokhin 1997) and  $\text{S}_2\text{O}_3^{2-}$  ions, and that under conditions of complete minerals flotation the value of the product  $[\text{FeOH}^+][X]$  should be constant. In this case the equations for calculation of the necessary xanthate ions concentration [X] value in pulp take the following from:

For pyrite:

$$\text{Log}[X] = [-0,29 + \text{log}[\text{FeOH}^+]] + 5/7.\text{pH} + 1/7.\text{log}[\text{S}_2\text{O}_3^{2-}] \quad (1)$$

For pyrrhotite:

$$\text{Log}[X] = [-1,98 + \text{log}[\text{FeOH}^+]] + 4/5.\text{pH} + 1/10.\text{log}[\text{S}_2\text{O}_3^{2-}] \quad (2)$$

The experimental relationship  $[X] = f(\text{pH})$  for chalcopyrite can be derived by the same way as in derivation of equation (1) and (2) for iron sulphides. The following equation is most suitable for the description of the experimental data (Figure 1)

For chalcopyrite:

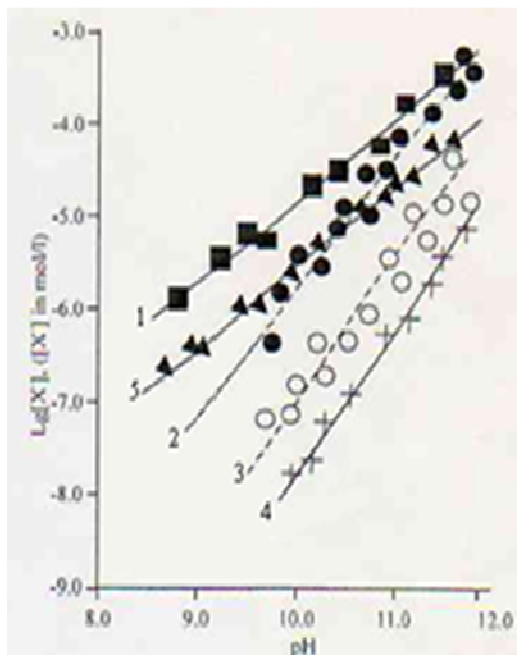
$$\text{Log}[X] = [-0,96 + 1/13.\text{log}[\text{Cu}^+][X]] + 12/13.\text{log}[\text{FeOH}^+][X]$$

$$+ 9/13.\text{pH} + 2/13.\text{log}[\text{SO}_3^{2-}] \quad (3)$$

If ethyl xanthate is used as collector the value of  $[\text{FeOH}^+][X] = K_0 = \text{const}$  is equal to  $3,5 \cdot 10^{-11}$  for pyrite and  $2,95 \cdot 10^{-12}$  for chalcopyrite. When butyl xanthate is used the values of  $K_0$  are approximately ten times lower. This is in agreement of the hydrocarbon chain length and the collector activity (Abramov, 1978). The different  $K_0$  values for the different iron sulphides indicate that the constancy of the product  $[\text{FeOH}^+][X]$  for each iron mineral is not derived from the following, for example, on the basis of iron xanthate or near the mineral surface.

Results of flotation investigations show (Figure 2) that the necessary concentration of X ions in flotation of activated sphalerite depends on the assay of isomorphous admixture of iron in its crystal lattice. It is less for white variety of sphalerite – cleiophane (Figure 2, curve 3) and much more for the black one – marmatite (Figure 2, curve 2). At the same time for both sphalerite varieties the similar regularity of the necessary  $[X] = f(\text{pH})$  changing with the change of pulp pH values is observed. Their inclined dependencies  $[X] = f(\text{pH})$  obtained for both sphalerite varieties (Figure 2, curve 2 and 3) coincide with those of covellite (Figure 2, curve 4).

It testifies that the composition of sulphide surface of activated sphalerite and covellite is alike. The difference in values of the necessary [X] in flotation of covellite, cleiophane and marmatite (Figure 2) is determined by influence of zinc sulphide underlying and isomorphous admixture of iron in it on thermodynamic properties of activating copper sulphide layer interacting with collector. However, at all pH values the necessary [X] even in flotation of marmatite very rich by iron is less (Figure 2, curve 2) than [X] necessary for complete flotation not



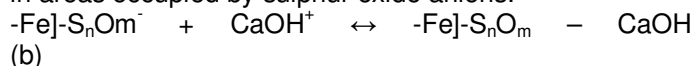
**Figure 2.** Effect of pH value on the required concentration (mol/l) of butyl xanthate [X] ensuring complete pyrite (1), marmatite (2), cleiophane (3), covellite (4), and chalcopyrite (5) flotation.

only pyrite (Figure 2, curve 1) but even of chalcopyrite at pH ≤ 10,5 (Figure 2, curve 5).

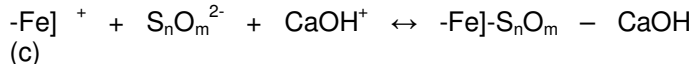
**Optimal conditions for depression of iron sulphides by lime.**

The [X] values calculated from equations (1) – (3) are practically independent of the ore deposit. However, they are accurate only when the concentration of calcium ions in the pulp is still insufficient for formation of calcium-bearing compounds on the iron and copper sulphide minerals surface. Existing hypothesis considering the formation of calcium sulphate, carbonate or hydrate as the main reason of pyrite depression by lime are in contradiction with facts of pyrite flotation in pulps saturated with respect to calcium sulphate (at Rommelsberg plant) or calcium carbonate [Abramov A. A., 1983]. “Cementation” hypothesis [Abramov A. A., 1978] turned out to be more correct.

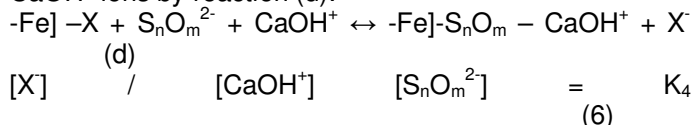
“Cementation” of the iron sulphides surface by calcium-bearing compounds is considered to be due to the chemical reaction of oxidation products of mineral sulphur on the surface with CaOH<sup>+</sup> ions according to reaction (b) in areas occupied by sulphur oxide anions:



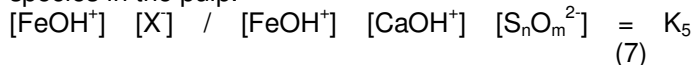
and according to reaction (c) in areas occupied by iron cations:



The possibility of “cementation” of the sulphide surface by calcium-bearing compounds in the presence of X<sup>-</sup> ions in the pulp will be determined by the relationship (6) between the concentration of X<sup>-</sup>, sulphoxide S<sub>n</sub>O<sub>m</sub><sup>2-</sup> and CaOH<sup>+</sup> ions by reaction (d):



Dividing and multiplying the left part of equation (6) by [FeOH<sup>+</sup>] allow to determine the ratio of conditions of flotation (the numerator of equation (7)) and depression of flotation (the denominator of equation (7)) of iron-containing sulphides in the presence of calcium-bearing species in the pulp.

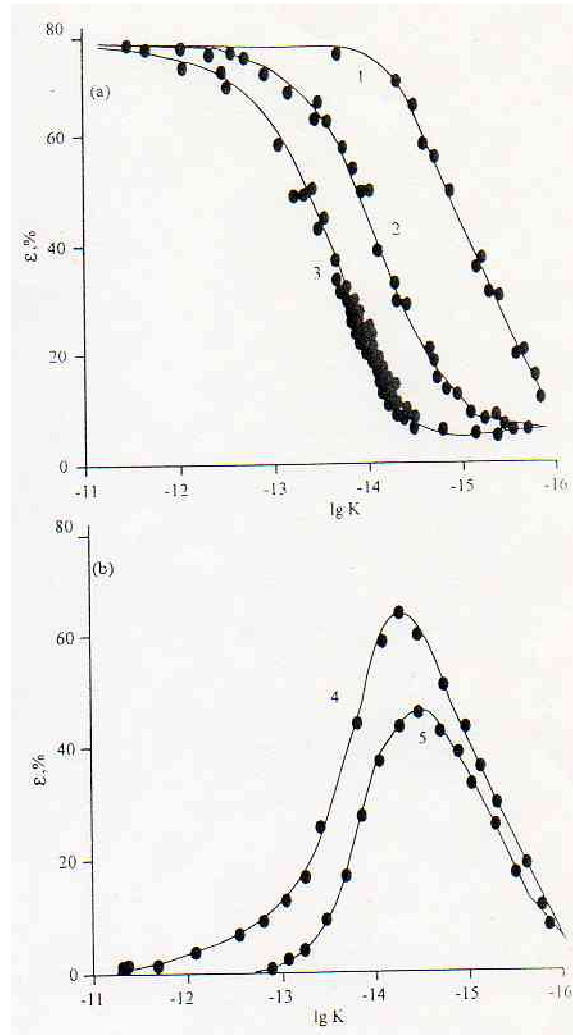


logarithming of the equation (7) and substituting into it the expression for [S<sub>n</sub>O<sub>m</sub><sup>2-</sup>] from equation (1) – (3) taking into account that [FeOH<sup>+</sup>][X<sup>-</sup>] = K<sub>0</sub> = const. enables to derive the relationship between the concentrations of X<sup>-</sup>, H<sup>+</sup> and CaOH<sup>+</sup> ions in the pulp

for the pyrite:  
 $\log[X^-] - 5/6.pH + 1/6.\log[CaOH^+] = \log K \quad (8)$

for pyrrhotite:  
 $\log[X^-] - 8/9.pH + 1/9.\log[CaOH^+] = \log K \quad (9)$

for chalcopyrite:



**Figure 3.** Effect of the lgK value (a) on chalcopyrite (1), pyrrhotite (2), and pyrite (3) floatability ( $\epsilon$ ) and (b) on the difference of chalcopyrite floatability ( $\epsilon$ ) as compared with the pyrite (4) and chalcopyrite (5) ones.

$\log[X] - 9/11 \cdot \text{pH} + 2/11 \cdot \log[\text{CaOH}^+] = \log K$  (10)  
 The value of these relationships will determine flotation or depression of iron-containing sulphides.

Results of the experimental verification of equation (8) – (10) in the laboratory and industrial conditions at Almalikskaya and Balkhashskaya copper-molybdenum plants (Figure 3) confirmed their validity.

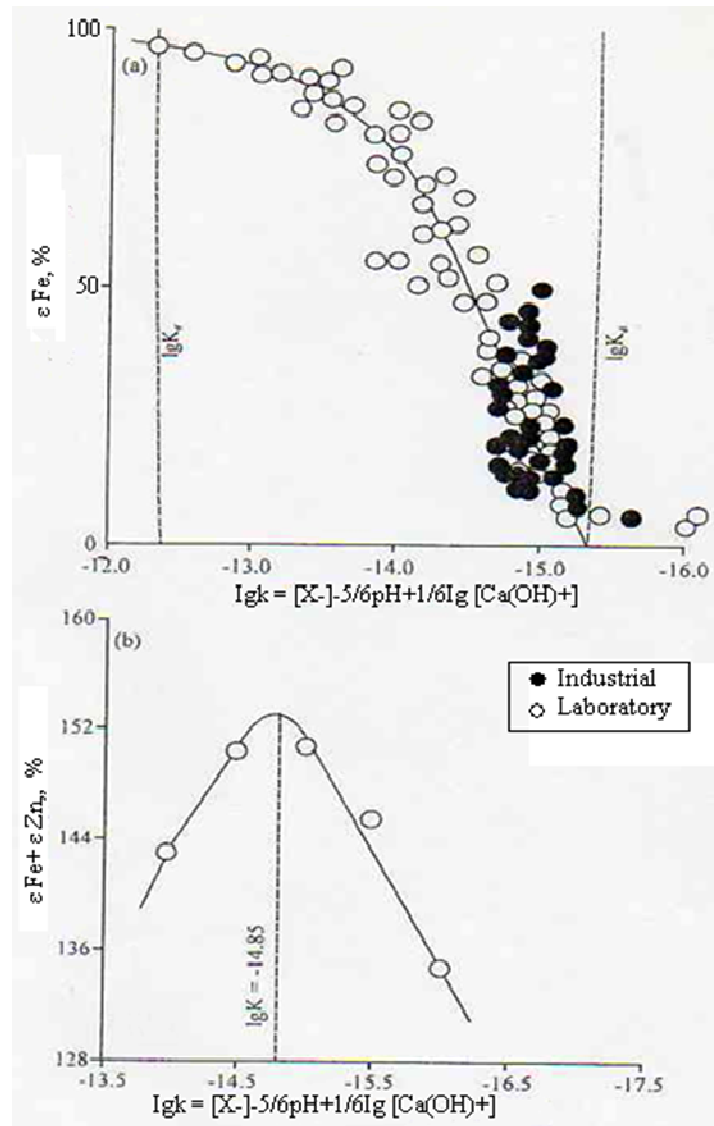
The value of logK for the complete depression of iron sulphides represented at the plants mainly by pyrite was -16,0 in all cases and the logK value corresponding to complete flotation of the above sulphides was -11,3 (Figure 3, a) in the presence of butyl xanthate and lime. The values of logK for the complete depression and flotation of pyrrhotite at this conditions were -15,8 and -13,3 and of chalcopyrite -16,0 and -14,2 correspondingly.

The maximum difference of chalcopyrite floatability and both iron sulphides, and the maximum selectivity of

their separation are observed at logK values near 14,3 - 14,6 (Figure 3, b).

Results of experimental verification of the equation (8) in zinc flotation circuits at Zaryanovskaya and Belousovskaya plants of polymetallic ores processing have proved its reliability too. Values of  $\log K_d$  for complete depression of iron sulphides represented mainly by pyrite in both cases made -12,3 and value of  $\log K_f$  answering their complete flotation -15,3 (Figure 4, a). Deviation of experimental data between boarder values of logK is quite natural and is determined by the difference of physical and chemical characteristics (for example, the oxidation degree) of the particular grains surface of iron sulphides in these conditions.

While investigation of optimal conditions for zinc flotation at Ziryanovskaya plant it has been established that the necessary calcium ions concentration for



**Figure 4.** Effect of the  $\lg K$  value on flotation recovery of iron sulphides ( $\epsilon$ ) in laboratory and industrial conditions (a) and on the total zinc and iron recovery in the rough zinc flotation at Zirianovskaya plant (b).

complete pyrite depression (at  $\log K = -15,3$ ) results in some depression of zinc sulphides too. Results of statistical treatment of data obtained by probing of zinc flotation circuit has shown (Figure 4, b) that maximum total zinc and iron recovery into concentrates of the same name is reached at the value of  $\log K = -14,85$ . Zinc recovery in the froth product in this case makes 75 %, iron 77 %.

By decreasing of  $\log K$  value, iron losses in the froth product and by its increasing- zinc losses into tailings of operation. In the cleaner operation, the contrary, it is necessary to maintain the value of  $\log K$  securing complete depression of pyrite and equalled -15,3 and only by this way, obtaining of the final zinc concentrate of the high quality is achieved. High zinc recovery in these

conditions is ensured by that non-floated sphalerite grains which are directed with tailings of the concentrate cleaning operation into the rough flotation with a softer regime of depression, pass into its concentrate and return into the cleaner operation.

Results of investigations at Zirianovskaya plant have shown also that in conditions of reagents consumption hand regulation great deviations of pulp ionic composition as compared with optimal one are observed. Values of  $\log K$  in the rough zinc flotation were changed from -14,5 to -15,3 having led to changes in recovery into the froth product: of zinc – from 62,6 to 92,6 % and iron – from 5,5 to 51,5 %. It is obvious that stabilization of optimal conditions for zinc flotation can be reached only by implementing automation control system at plants and

using the derived relationships (physico-chemical models) as criteria for its functional control units.

## CONCLUSIONS

Theoretical considerations have resulted in the development of quantitative relationships between concentrations of xanthate, hydrogen and calcium – bearing ions corresponding to conditions of complete flotation and depression of copper, zinc and iron sulphide minerals. Reliability of relationships derived has been confirmed by laboratory and industrial conditions.

Determined conditions for complete (maximum) flotation or, alternatively, for complete depression are equally accurate for minerals from various deposits. Therefore, the quantitative relationships derived for optimal conditions of copper and zinc sulphides flotation and depression of iron sulphides by lime can be used for two ways: firstly, for analysis and improving the process of copper and zinc sulphides selective flotation from copper – pyrite or polymetallic ores and, secondly, as physico-chemical models for functional units of automation control

systems for regulation of these processes at ore-dressing plants.

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