

THERMODYNAMIC MODELS FOR DEPRESSION OF PYRITE BY LIME IN COPPER AND ZINC FLOTATION

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ABSTRACT

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 processes.

minerals under investigation and comparison of the results received with experimental data. The methodology of the thermodynamic analysis 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 physico-chemical 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 of these processes at the concentration plants.

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

INTRODUCTION

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

The main reason why industrial plants can not obtain maximum flotation performance is caused by changing in the composition of ores and concentrates treated. The only practical way to compensate such variations at the concentration plants is regulation of the reagents consumption in flotation.

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 the possible reactions of collector in the vicinity of the surface of

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 Belousovskoe deposits have been used. Results of their flotation have shown that it depends sharply on pH values (Fig.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.

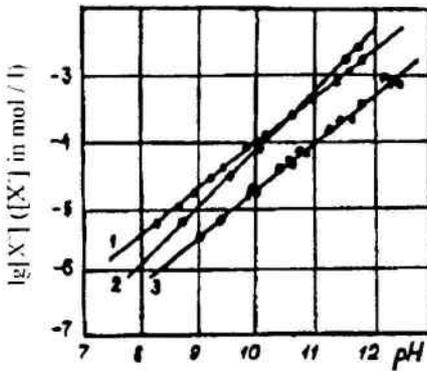


Figure 1. Effect of pH value on the required concentration (mol/l) of ethyl xanthate [X] ensuring maximum pyrite (1), pyrrhotite (2) and chalcopyrite (3) flotation.

Relationships between xanthate X^- and hydrogen H^+ ions concentrations $[X^-] = f(pH)$ ensuring maximum 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 hydroxo-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 $[X^-] = f(pH)$ received for pyrite and pyrrhotite (Fig.1) can be explained by assuming that the necessary $[X^-]$ value is determined by the $[FeOH^+]$ value in the vicinity of the surface during the conversion of FeS_2 and FeS to $Fe(OH)_3$ (the basic product of iron sulphides oxidation) (Abramov and Avdohin 1997) and $S_2O_3^{2-}$ ions, and that under conditions of complete minerals flotation the value of the product $[FeOH^+][X^-]$ should be constant. In this case the equations for calculation of the necessary xanthate ions concentration $[X^-]$ value in pulp take the following form:

for pyrite:

$$\lg[X^-] = [-0.29 + \lg[FeOH^+][X^-]] + 5/7 \text{ pH} + 1/7 \lg[S_2O_3^{2-}] \quad (1)$$

for pyrrhotite:

$$\lg[X^-] = [-1.98 + \lg[FeOH^+][X^-]] + 4/5 \cdot \text{pH} + 1/10 \cdot \lg[S_2O_3^{2-}] \quad (2)$$

The experimental relationship $[X^-] = f(pH)$ for chalcopyrite can be derived by the same way as in

derivation of equations (1) and (2) for iron sulphides. The following equation is most suitable for the description of the experimental data (Fig.1)

for chalcopyrite:

$$\lg[X^-] = [-0.96 + 1/13 \cdot \lg[Cu^+][X^-]] + 12/13 \cdot \lg[FeOH^+][X^-] + 9/13 \cdot \text{pH} + 2/13 \lg[S_2O_3^{2-}] \quad (3)$$

If ethyl xanthate is used as collector the value of $[FeOH^+][X^-] = K_0 = \text{const}$ is equal to $3.5 \cdot 10^{-11}$ for pyrite, $1.4 \cdot 10^{-10}$ for pyrrhotite 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 with the theoretical conception of influence of the hydrocarbon chain length on the collector activity (Abramov, 1978). The different K_0 values for the different iron sulphides indicate that the constancy of the product $[FeOH^+][X^-]$ for each iron mineral is not derived from the formation, for example, of basic iron xanthate on or near the mineral surface.

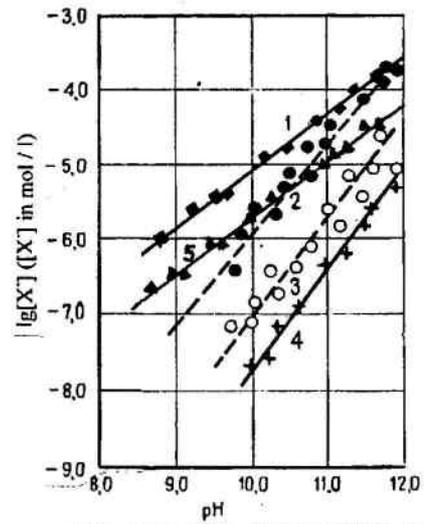


Figure 2. Effect of pH value on the required concentration (mol/l) of butyl xanthate [X] ensuring complete pyrite (1), marmatite (2), cleiophane (3), covellite (4) and chalcopyrite (5) flotation.

Results of flotation investigations show (Fig.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 (Fig.2, curve 3) and much more for the black one – marmatite (Fig.2, curve 2). At the same time for the both sphalerite varieties the similar regularity of the necessary $[X^-]$ changing with the change in pH values of pulp in flotation is observed. By their inclination dependencies $[X^-] = f(pH)$ received for both sphalerite varieties (Fig.2, curves 2 and 3)

coincide with those for covellite (Fig.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, cleiofane and marmatite (Fig.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 (Fig.2, curve 2) than $[X^-]$ necessary for complete flotation not only pyrite (Fig.2, curve 1) but even of chalcopyrite at $\text{pH} \leq 10.5$ (Fig.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.

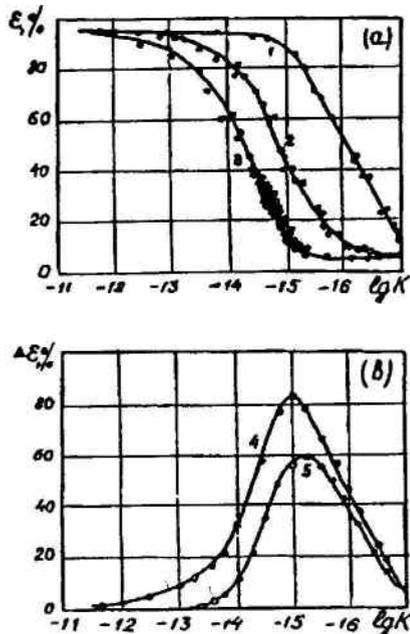


Figure 3. Effect of the $\lg K$ value (a) on chalcopyrite (1), pyrrhotite (2) and pyrite (3) floatability (ϵ) and (b) on the difference of chalcopyrite floatability (ϵ) as compared with the pyrite (4) and pyrrhotite (5) ones

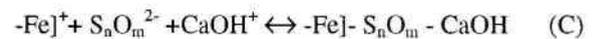
Existent hypotheses considering the formation of calcium sulphate, carbonate or hydrate as the main reason of pyrite depression by lime are in contradiction with facts of pyrite flotation in pulps saturated with

respect to calcium sulphate (at Rommelsberg plant) or calcium carbonate (Abramov, 1983). «Cementation» hypothesis (Abramov 1978) turned out to be more correct.

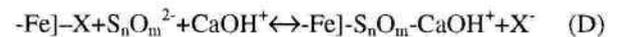
«Cementation» of the iron sulphides surface by calcium-bearing compounds is considered to be due to the chemical reaction of oxidation products of mineral sulphur on the surface with CaOH^+ ions according to reaction (B) in areas occupied by sulphur oxide anions:



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^- ions in the pulp will be determined by a relationship (6) between the concentration of X^- , sulphoxide $\text{S}_n\text{O}_m^{2-}$ and CaOH^+ ions by reaction (D):



$$[X^-] / [\text{CaOH}^+] [\text{S}_n\text{O}_m^{2-}] = K_4 \quad (6)$$

Dividing and multiplying the left part of equation (6) by $[\text{FeOH}^+]$ 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.

$$[\text{FeOH}^+] [X^-] / [\text{FeOH}^+] [\text{CaOH}^+] [\text{S}_n\text{O}_m^{2-}] = K_5 \quad (7)$$

Logarithming of the equation (7) and substituting into it the expression for $[\text{S}_n\text{O}_m^{2-}]$ from equations (1) - (3) taking into account that $[\text{FeOH}^+] [X^-] = K_0 = \text{const.}$ enables to derive the relationship between the concentrations of X^- , H^+ and CaOH^+ ions in the pulp

for pyrite:

$$\lg [X^-] - 5/6 \cdot \text{pH} + 1/6 \cdot \lg [\text{CaOH}^+] = \lg K \quad (8)$$

for pyrrhotite:

$$\lg [X^-] - 8/9 \cdot \text{pH} + 1/9 \cdot \lg [\text{CaOH}^+] = \lg K \quad (9)$$

for chalcopyrite:

$$\lg [X^-] - 9/11 \cdot \text{pH} + 2/11 \cdot \lg [\text{CaOH}^+] = \lg K \quad (10)$$

The value of these relationships will determine flotation or depression of iron-containing sulphides.

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

The value of $\lg K$ for the complete depression of iron sulphides represented at the plants mainly by pyrite was -15.2 in all cases and the $\lg K$ value corresponding to complete flotation of the above sulphides was -11.8 (Fig. 3, a) in the presence of butyl xanthate and lime. The values of $\lg K$ for the complete depression and flotation of pyrrhotite at this conditions were -16.2 and -13.3 and of chalcopyrite -17.0 and -14.8 correspondingly.

The maximum difference in floatability of chalcopyrite and both iron sulphides and therefore the maximum selectivity of their separation are observed at near $\lg K$ values equaled 15.0-15.2 (Fig. 3, b).

Results of experimental verification of the equation (8) in zinc flotation circuits at Zirianovskaya and Belousovskaya plants processing polymetallic ores have proved its reliability too. Values of $\lg K_d$ for complete depression of iron sulphides represented mainly by pyrite in both cases made -15.2 and value of $\lg K_f$ answering their complete flotation -11.8 (Fig.4, a). Deviation of experimental data between boarder values of $\lg K$ is quite natural and is determined by the difference in physico - chemical characteristics (for example, the oxidation degree) of the surface of particular grains of iron sulphides in these conditions.

While investigation of optimal conditions for zinc flotation at Zirianovskaya plant it has been established that the necessary for complete depression of pyrite flotation the calcium ions concentration (at $\lg K = -15.2$) results in some depression of zinc sulphides too. Results of statistical treatment of data received in probing of the zinc flotation circuit has shown (Fig.4, b) that maximum total zinc and iron recovery into concentrates of the same name is reached at the value of $\lg K = -14.85$. Zinc recovery in the froth product in this case makes 74 - 77%, iron - 20 - 30%.

In decreasing of $\lg K$ value iron losses in the froth product are increased and in its increasing - zinc losses into tailings of the operation. In the cleaner operation, on the contrary, it is necessary to maintain the value of $\lg K$ securing complete depression of pyrite and equaled -15.2 as only by this a way reception of the final zinc concentrate of the high quality is achieved. High zinc recovery in this conditions is ensured by that non-floated sphalerite grains are directed with tailings of the concentrate cleaner into the rough flotation with a

more soft regime of depression, pass into its concentrate and are returned into the cleaner operation.

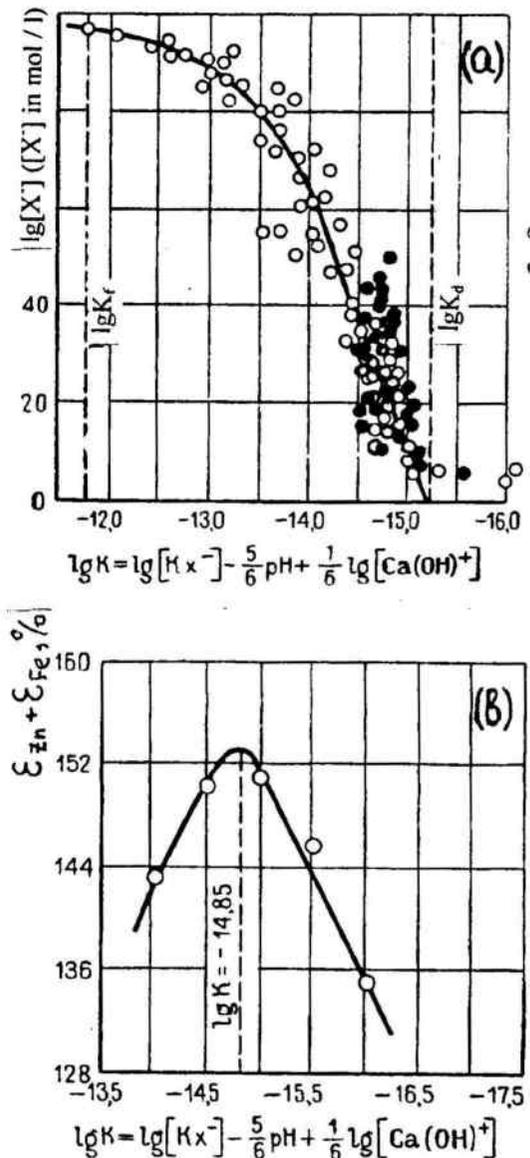


Figure 4. Effect of the $\lg K$ value on flotation recovery of iron sulphides (ϵ) in laboratory (1) and industrial (2) conditions (a) and on the total zinc and iron recovery in the rough zinc flotation at Zirianovskaya plant (b).

Results of investigations at Zirianovskaya plant have shown also that in conditions of hand regulation of reagents consumption grate deviations of the pulp ionic composition as compared with the optimum one are observed. Values of $\lg K$ in the rough zinc flotation were changed from -14.5 to -15.5 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 in implementation at plants of the automation control system using derived relationships (physico – chemical models) as the criterion 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 under laboratory and industrial conditions.

Conditions determined 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 at depression of iron sulphides by lime can be used in 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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