

Action selectivity of consecutive use of collectors during flotation of copper-zinc ore

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Abstract

Today selective flotation of copper-zinc-pyrite ores at deterioration of the technological properties of raw material is one of the most important problem. The solution of this problem involves the use of more selective collectors combined with the main reagent-collector – xanthate. The article presents the study results of competing adsorption of butyl xanthate and dithiophosphate BTF-1541 on non-activated sphalerite. Discovered dependences of flotation of chalcopyrite, sphalerite and pyrite with xanthate and dithiophosphate combinations depending on the pH of the pulp, which had allowed establishing the optimal proportions of collectors for each cycle of collectively selective flotation were described. Extraction of zinc using xanthate during ore processing according to scheme adopted on the factory is not more than 53%. As a result of changes in reagent regime, reduction of zinc losses in the copper cycle by 3.64% and a more complete extraction of metals in the same name concentrates were obtained. Recovery of copper in copper concentrate was increased by 2.84%, zinc extraction in the zinc concentrate – by 13.25%.

Keywords: FLOTATION, SELECTIVITY, COPPER-ZINCORES, SODIUMDITHIOPHOSPHATE, COLLECTORS COMBINATIONS

Introduction

Mineral resources base of non-ferrous metallurgy plays an important role in the development of Russia's industrial potential. Currently, Russia is among the leaders in terms of reserves of copper and zinc. Russia is in fifth place in the world at copper production (about 10% of world reserves). Russian zinc reserves amount to 20% of the world ones, at its extraction and production Russia occupies the sixth place [1].

The basis of the Russian copper resource base is copper-nickel sulfide deposits (Norilsk ore area – Oktyabrskoye, Talnakhskoye) and pyrite deposits (copper and copper-zinc located in the Southern and Middle Urals, in Orenburg and Chelyabinsk regions).

The main process of ore dressing, in which as valuable metals copper and zinc are used, is a flotation, and only a small part of them is subjected to metallurgical processing or beneficiation by other methods. At the same time, the quality of copper and zinc concentrates is determined by a number of dominant factors. Decrease in the content of useful components in the mineral raw materials, complex material composition, very fine disseminations of sulphide minerals in each other and in the gangue, unfavorable for the selective flotation copper and zinc ratio (1:2 - 1:0.5),

proximity of technological properties of ore-forming minerals are more often observed.

According to mineral composition pyrite ores are very diverse. The main valuable minerals are chalcopyrite (also secondary sulfides and copper sulfates occur) and sphalerite, pyrite is a main ore mineral, which content sometimes reaches 90%. Physical properties of the main ore minerals, which characterize technological properties of ore in general, pH and ionic composition of the pulp liquid phase, concentration of copper ions, type, reagents consumption and other factors predetermine the behavior of the minerals in the beneficiation processes. Therefore, the problem of selective sulphide flotation separation of non-ferrous metals from iron sulfide, and then selective flotation separation of collective concentrate in the beneficiation of disseminated copper-zinc ores of complex composition is one of the most difficult tasks.

Constantly growing demand for marketable concentrate quality makes researchers and scientists around the world search various ways to improve the beneficiation technology [2, 3], as well as to develop a fundamentally new reagent regimes with a more efficient, effective and low-toxic flotation reagent of

selective action [4, 5]. Many well-known scientists from the middle of the 20th century [6, 7, 8] have been engaged in the development of selective reagent regimes for flotation of copper-zinc ores in our country. Even then, to use combinations of collectors (strong and weak) was considered as rational approach. In the period of “perestroika” (restructuring) and up to date in connection with the closure of plants producing the original chemical raw materials production of certain effective flotation reagents has stopped. However, contrary to the current situation, the domestic chemical industry produces enough range of reagents for flotation processing of ores of non-ferrous metals. As the base-collector agent in the flotation of sulphide ores butyl xanthate of potassium, as well as several types of dialkyldithiophosphates, without which it is difficult to obtain high-quality concentrates, are applied. Collectors are used either separately in different cycles flotation [9] or together in different ratios [10, 11].

The objective of this work is to investigate the consistent application of sulfhydryl collectors to increase the selectivity and completeness of the valuable metals recovery from the copper-zinc-pyrite deposits of Urals.

Materials and methods of research

Carried out research of froth flotation comprises fine crushing by dry method of mono-mineral fractions of sulfides: chalcopyrite, sphalerite and pyrite with allocation of class $-0.08 + 0.04$ mm, which is directed to a flotation unit with chamber volume of 20 ml. Flotation was carried out at different pH produced by lime.

Research by IR spectroscopy method* was conducted to study the collectors and clarify the mechanisms of their interaction with the surface of sphalerite. Registration and processing of the IR spectra of reagents and mineral powder of sphalerite was performed with FTIR using spectrometer IRAffinity-1 made by firm «SHIMADZU» in a wave number range of 400-4000 cm^{-1} with definition of 4 cm^{-1} .

Technological research was carried out on ore sample of Yubileynoe deposit with unfavorable ratio of copper and zinc 1:1, with a mass fraction of copper - 2.21%, zinc - 2.13%. The experiments were conducted on adopted at Haybullinskoy dressing plant selective-collective-selective scheme with the release of inter-cycle flotation concentrate.

As sulfhydryl collectors potassium butyl xanthate and sodium dialkyldithiophosphate (BTF-1541) as well as their combinations in different proportions were

used. During the technological tests the reagent regime provided feed of sphalerite depressors in the copper cycle: zinc sulphate and sodium sulfide, in the zinc cycle – copper sulfate.

Results and discussion

To describe the interactions of flotation reagents with sulfide minerals in the flotation process, it was required to conduct research in several stages. The study of competing adsorption of xanthate and dialkyldithiophosphate in the non-activated sphalerite containing no cations with variable valence, where according to the concept [12] diksantogen cannot be formed, is of considerable interest. Interaction of xanthates and dialkyldithiophosphates with the surface of sulfide minerals in the literature is considered from the standpoint of the formation of surface compounds with coordinate bond, which is formed on the donor-acceptor mechanism by transferring an electron pair from donor-flotation reagent to acceptor-mineral. There are two types of possible interactions: an electron-donor-acceptor (redox) reactions and donor-acceptor interaction accompanied by the exchange of particles, ions, atoms and molecules (ion exchange reactions) [13]. Sorption optimum of reagents of non-sulfide minerals depending on the pH of the medium in most cases coincides with the optimum complex formation cation of lattice mineral with a reagent in solution. However, in real systems, there may be some deviations from the theoretical values, and it is necessary to study the absorption of dialkyldithiophosphate as a part of the real reagent in little-activated and non-activated sphalerite of developing pyrite deposits. One of the most promising methods for studying solutions and solids – FTIR spectrometry method was applied to the study.

There are bands corresponding to the stretching vibrations C-H according to the analysis of dialkyldithiophosphate IR spectrum of reagent BTF 1541 (Fig. 1, a) in the highest frequency area of 3000-2840 cm^{-1} . Intense absorption band in the infrared spectrum of the reagent in the area of 3449 cm^{-1} should be attributed to fluctuations of O-H group. Three absorption bands of different intensity at 2974, 2936 and 2889 cm^{-1} correspond to the stretching vibrations of C-H bond. Three bands at 1234, 1138 and 1107 cm^{-1} correspond to the stretching vibrations of P-O-C bonds. Intense bands at wave numbers range of 750-580 cm^{-1} belong to stretching vibrations of P=S (752 and 671 cm^{-1}) bonds, 563 and 474 cm^{-1} – P-S bond vibrations.

The spectrum of xanthate (Fig. 1, a) contains the characteristic frequencies of stretching vibrations of

* Registration of IR spectra was performed by Ph.D. M. V. Ryazantseva (IPKON RAS)

C-H bond ($2959, 2947 \text{ cm}^{-1}$), deformation vibrations of CH_3 and CH_2 groups (asymmetric - 1450 , symmetric - 1389 cm^{-1}), skeletal vibrations of CH_3 (1234 cm^{-1}) and CH_2 (748 cm^{-1}) groups. Band at 2874 cm^{-1} characterizes CH-O bond. The most intense bands in

the range of wave numbers 1258 and 1022 cm^{-1} relate to stretching vibrations of $\text{C}=\text{S}$ bonds, and spectra in the range of $750\text{-}550 \text{ cm}^{-1}$ – to C-S bonds. When 1234 and 1138 cm^{-1} stretching vibrations of C-O-C bond are shown.

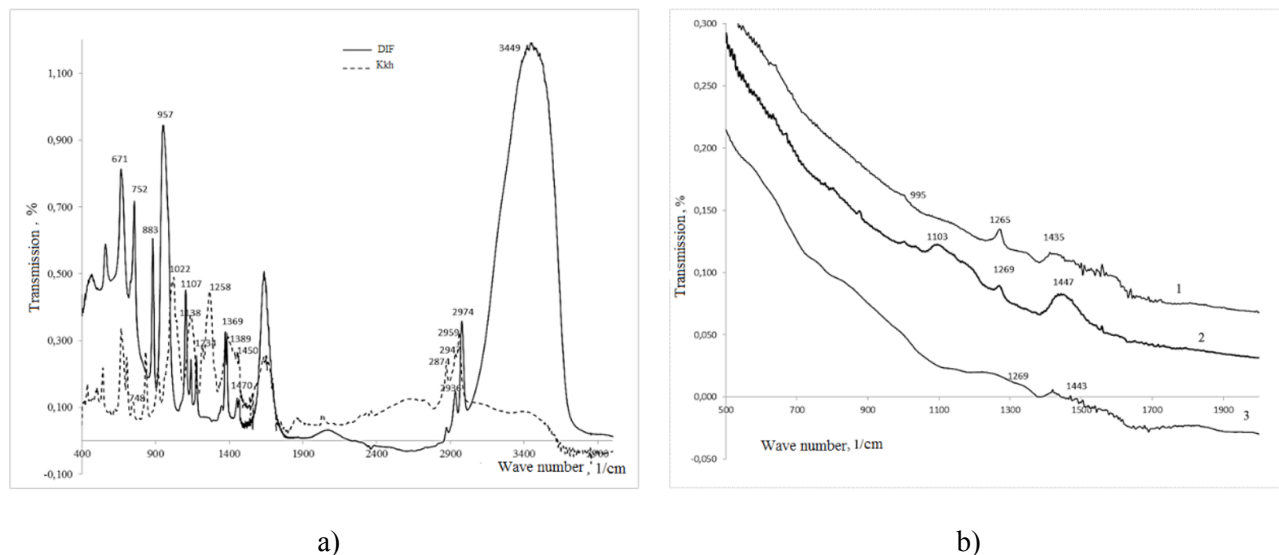


Figure 1. FTIR spectra:

a) an aqueous solution of dialkyldithiophosphate (BTF-1541) and butyl xanthate; b) sphalerite processed by dialkyldithiophosphate, 100 g/t (1); pure sphalerite (2); sphalerite processed by xanthate, 100 g/t (3)

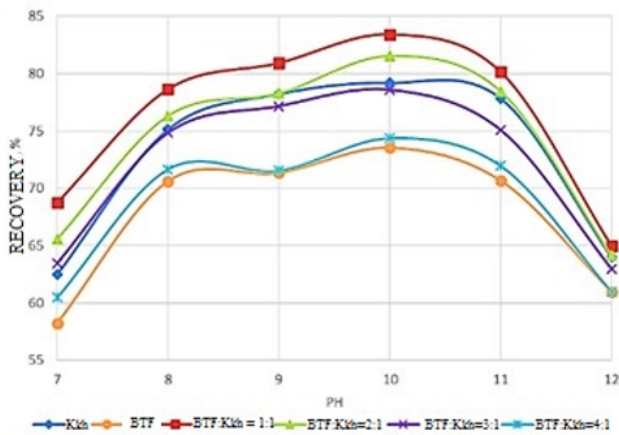
Fig. 1b - (2) shows main peaks in the area of $1500\text{-}1200 \text{ cm}^{-1}$ corresponding to zinc sulfide. A comparison of the IR spectra of sphalerite unprocessed with reagents, and sphalerite after agitation with dithiophosphate at $\text{pH} = 9$, there is a complete compliance of peaks with their slight shift to the short-wavelength area. This may indicate the adsorption interaction of the reagent with the mineral. In the IR spectrum of sphalerite processed by xanthate, peaks characterizing belaying of reagent on the mineral surface are not observed. One possible reason for obtaining the weak absorption bands can be insufficient reagents concentration. Nevertheless, comparing the action of reagents with each other, it can be noted that the lower concentration is required for interaction with aerofloat mineral.

It is known that at different pH values, collector adsorption on the mineral surface is very changeable. To obtain new scientific data on the conditions conducive to the two collectors are optimally adsorbed on the mineral surface, it has been required to conduct a series of experiments at different pH values of the liquid phase. As can be seen from Fig. 2 (a) dithiophosphate is a weaker collector of chalcopyrite in all investigated pH than xanthate. Such weak collective action of dithiophosphates compared to xanthate is associated with their more difficult oxidation

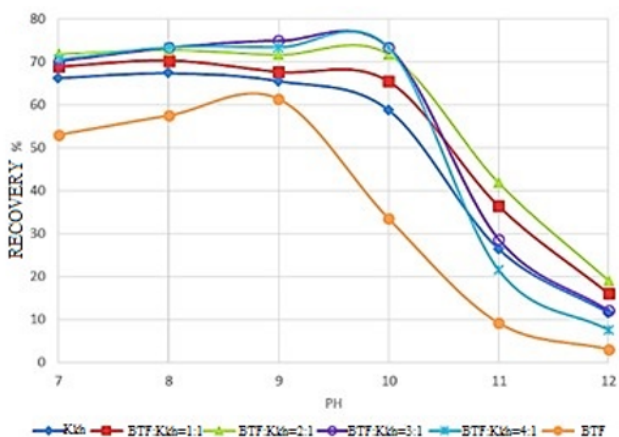
to disulfides [14].

Using a combination of reagents in all four ratios leads to greater copper mineral flotation throughout the pH range. The maximum values in the recovery of copper to concentrate (78-83%) are achieved with a ratio of reagents of 2:1 and 1:1 in the range of values $\text{pH}=9\text{-}10$.

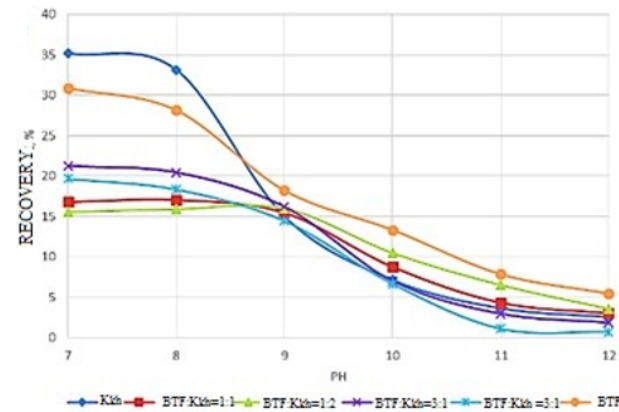
In fig. 2 (b), reagent BTF demonstrates clearly their selective properties relative to sphalerite over the pH range studied. In neutral and weakly alkaline environments (up to $\text{pH}=10$), feeding of two collectors increases floatability of sphalerite compared to xanthate. The larger share of aerofloat in the mixture, the higher the curves on the graph. In strongly alkaline medium, sphalerite is slightly floated at extraction level of 3-19% (maximum zinc recovery is at collectors ratio of 2:1). Application of a BTF pyrite reagent during flotation (Fig. 2c) at pH area up to 8.5 leads to a reduction of pyrite recovery by 5% and while increasing the alkalinity of the pulp liquid phase, it exhibits stronger collecting properties than xanthate. Partial replacement of xanthate by aerofloat in slightly alkaline medium ($\text{pH} = 7\text{-}9$) provides a huge reduction in the flotation of pyrite (by 20% at 2:1 ratio). In alkaline medium, the smallest flotation of iron sulfide is observed when a decrease in the proportion of xanthate.



a)



b)



c)

Figure 2. Extraction of minerals during flotation by collectors combinations in different media:

a - chalcopyrite, b – sphalerite, c– pyrite

Turning to the practice of processing the copper-zinc ores, the optimum alkalinity of the pulp in the allocation of inter-cycle flotation concentrate and flotation of copper minerals cycle is maintained in the range of pH= 7-10. Based on the above-described patterns of copper and zinc sulfides flotation (Fig. 2a

and b), it can be assumed that in the cycle of copper flotation for maximum recovery of copper minerals in the concentrate with minimum losses of zinc the supply of BTF-1541 collectors and butyl xanthate in ratio 1:1 will be considered relevant. Considering the collective flotation cycle, the bulk of pyrite should be removed with final tailings with minimum losses of valuable metals. According to the results of these studies the optimal boundary value of the medium is pH = 10. The ratio of collectors in this case can be from 3:1 to 4:1. In Fig. 3, the difference in the sphalerite and pyrite flotation collectors and their combinations is shown to determine the optimal conditions for conducting the zinc flotation cycle maintained in an alkaline medium. It is found that the maximum selectivity of the flotation is observed at pH = 10. With the prevalence of dithiophosphate proportion in the collectors mixture pyrite floats by 66% less than sphalerite.

And when pH = 11 a difference in extraction of sulfides reduces. In such conditions for a better selection, it is necessary to reduce the proportion of dithiophosphate in composition. In strongly alkaline medium (pH = 12), sphalerite extraction is only by 15% more than recovery of pyrite during flotation with collectors in a ratio of 2:1.

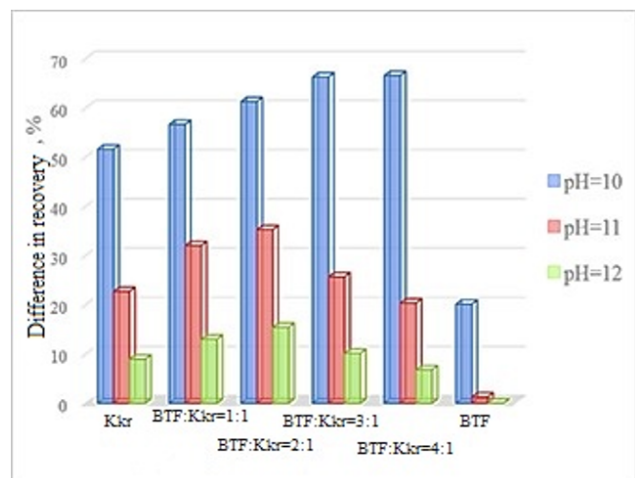


Figure 3. The difference in flotation of zinc and iron sulfides with collectors and their combinations in an alkaline medium

However, the flotation behavior of copper-zinc ores minerals is determined not only by their natural properties but also by reagent regime typical for a certain cycle of flotation. For example, in copper flotation cycle for sphalerite depression, zinc sulfate and sodium sulfide are used, and in zinc flotation sphalerite is pre-activated with copper sulfate. Therefore, this study was continued in carrying out open and closed experiments when flotation of ore sample in conditions of water rotation and use of additional

modifiers, taking into account all factors occurring at the same time.

Two collectors ratio (1:1 and 1.5:1) were considered. For comparison, an experiment with a xanthate as a collector was carried out. The results of experiments in an open cycle indicate the effectiveness of

the studied composition of collectors even at the stage of supply into the "head" of the process: copper recovery in concentrate of inter-cycle flotation is increased by 6.78% with an increase in the copper content by 0.9% (Fig. 4.).

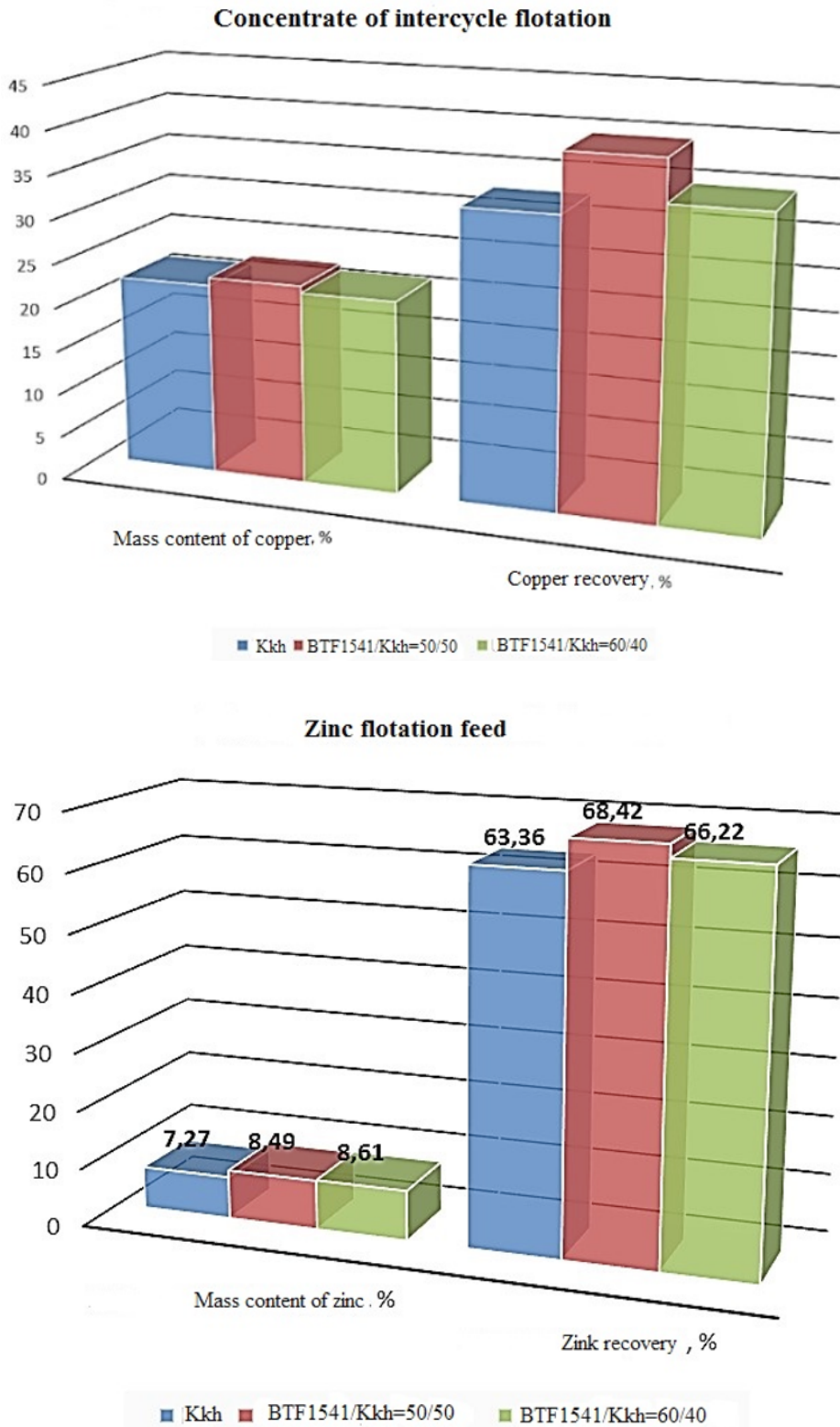


Figure 4. Effect of the ratio of main collector Kkh and addition collector BTF on technological parameters of flotation

The total copper concentrate was obtained with a high content of copper without loss of extraction (extraction is maintained at 82%) when using equal proportions of two collectors. The efficiency and selectivity of the process except for the process indicators are determined by the selectivity criteria. One of the most common is the selectivity factor, which according to K. F. Beloglazov is defined by the following equation:

$$S = \frac{1 - \varepsilon_{Cu}}{1 - \varepsilon_{Zn}},$$

where ε_{Cu} , ε_{Zn} – copper and zinc recovery into the foam product, %.

The results of calculation, the coefficient for inter-cycle flotation operation and for copper cycle showed (Table 1) that its values were considerably increased when using two collectors in the ratio 1:1.

Table 1. Selectivity factor according to K. F. Beloglazov

Name of the operation technological scheme	Collectors ratio BTF:Kkh		
	Kkh	1:1	1.5:1
Inter-cycle flotation	11.96	12.21	12.16
Copper cycle	6.66	7.29	7.10
Zn flotation feed	12.90	15.13	13.89

It is important to emphasize that there is an increase in selection of copper and zinc sulphides and zinc flotation feed. This indicates that the combination of BTF with xanthate in specified proportions allows reducing the losses of zinc in the copper cycle, and thus directs to a zinc flotation richer sphalerite product containing by 5% more zinc (Fig. 4). Therefore, it is possible to obtain a zinc concentrate with an increase in zinc recovery by 4.46% and 5.05% richer.

To confirm the identified patterns, the laboratory experiments were conducted in a closed cycle under the same conditions (Table 2). From the data of Table 2, it follows that equal feed of two collectors provides obtaining the copper concentrate with a copper content of 19.41%, zinc of 2.64% when copper recovery is 86.9% and the selectivity factor of copper and zinc minerals separation is 5.46. Using butyl xanthate, the copper concentrate containing 18.27% of copper, 2.83% of zinc when copper recovery of 84.06% has been obtained; selectivity coefficient of copper and zinc minerals separation is 4.28.

As a result of the joint use of sodium dithiophosphate and butyl xanthate during flotation of ore with an unfavorable ratio of copper and zinc we managed to avoid significant losses of sphalerite in collective and copper cycles of flotation and convert it into the final concentrate in the cycle of zinc flotation.

Table 2. Effect of collectors ratio on technological performances of flotation

Product	Yield, %	Mass content, %		Recovery, %	
		copper	zinc	copper	zinc
<i>Butyl xanthate</i>					
Con. of int.-cycl. flotation	3.24	23.50	2.50	39.77	6.63
Total Cu con.	8.81	18.27	2.83	84.06	20.38
Zinc con.	2.05	3.00	32.11	3.21	53.84
<i>BTF1541 / Bkh=50/50</i>					
Con. of int.-cycl. flotation	3.44	23.86	2.27	39.44	5.31
Total Cu con.	9.32	19.41	2.64	86.90	16.74
Zinc conc.	2.98	2.50	33.12	3.58	67.09
<i>BTF1541 / BKh=60/40</i>					
Con. of int.-cycl. flotation	3.20	23.20	2.41	38.83	5.78
Total Cu con.	8.86	18.11	2.80	83.93	18.56
Zinc con.	2.66	3.02	30.42	4.20	60.61

Conclusions

As a result of complex research, it was found that consistent application of the sodium dialkyldithiophosphate and xanthate have the greatest hydrophobizate effect on the minerals of copper and zinc while

hydrophiling the pyrite surface. The optimal proportions of reagents for each cycle of the collective-selective flotation of copper-zinc ores have been determined: in the copper cycle the collectors feed in the same amount is recommended and in the collective and

zinc cycles it is suggested to increase the proportion of aerofloat (3:1 to 4:1). The studied copper-zinc-pyrite ore from one of the Urals deposits is characterized by low technological properties. Recovery of zinc during ore processing by scheme adopted at plant using xanthate is not more than 53%. As a result of changes in reagent regime reduction of zinc losses in the copper cycle by 3.64% and a more complete extraction of metals in concentrates of the same name were obtained. Extraction of copper in the copper concentrate increased by 2.84%, zinc recovery in the zinc concentrate - by 13.25%.

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References

1. Benevolsky B. I., Migachev I. F. (2013) Sostoyanie mineralno-syirevoy bazyi tsvetnykh metallov Rossii i osnovnyie napravleniya geologorazvedochnykh rabot [State of the mineral resource base of non-ferrous metals in Russia and the main directions of prospecting works]. *Razvedka i ohrana nedr* [Exploration and protection of mineral resources]. No. 4. p.p. 28-31.
2. Kohad V.P. (1998) Flotation of Sulphide Ores – HZL Experience. Froth flotation: recent trends. Lime. Jamshedpur. p. p. 18-41.
3. Bulatovic S., Wyslouzil D.M. (1995) Selection and evaluation of different depressants systems for flotation of complex sulphide ores. *Minerals Engineering*. Vol. 8. Issues 1–2. p. p. 63-76.
4. Soltani F., Koleini S. M. J. (2014) Abdollahy M. Optimization of Cu–Zn massive sulphide flotation by selective reagents. *Journal of The Institution of Engineers (India): Series D*. October 2014, Vol. 95, Issue 2, p. p. 125–134.
5. Lotter N.O., Bradshaw D.J. (2010) The formulation and use of mixed collectors in sulphide flotation. *Minerals Engineering*. Vol. 23. Issues 11–13. p. p. 945–951.
6. Kisliakov L. D., Kozlov G. V., Nagirnyak F. I. (1966) *Flotatsiya medno-tsinkovykh i mednykh rud Urala* [The flotation of copper-zinc and copper ores of the Urals]. Moscow: Nedra. 387 p.
7. Abramov A. A., Leonov S. B. (1991) *Obogashchenie rud tsvetnykh metallov. Ucheb. dlya vuzov* [Beneficiation of ores of nonferrous metals. Proceeding for high schools]. Moscow: Nedra. 407 p.
8. Kakovskiy I. A., Komkov V.D. (1970) Issledovanie flotatsionnykh svoystv ditiyofosfatov [Research of dithiophosphates flotation properties]. *Izvestiya VUZov. Gornyy zhurnal* [Proceedings of the universities. Mining Journal]. No.11. p.p. 181-186.
9. Asonchik K. M., Polkin V. N., Starostin Yu. I., Repina N. V., Ryaboy V. I. (2006) Povyshenie kachestva mednogo kontsentrata pri flotatsii medno-tsinkovykh rud Gayskogo mestorozhdeniya [Improving the quality of copper concentrate during flotation of copper-zinc ores of Gaiskiy deposits]. *Obogashchenie rud* [Ore dressing]. No 6. p.p. 7-9.
10. Ryaboy V. I., Shenderovich V. A., Kretov V. P. (2005) Primenenie aeroflotov pri flotatsii rud [Application of aerofloats in the flotation of ores]. *Obogashchenie rud* [Ore dressing]. No. 6. p.p. 43-44.
11. Ignatkina V. A., Bocharov V. A., Sabanova M. N., Orekhova N. N. (2012) Selektivnyy reagentnyy rezhim flotatsii kolchedannoy medno-tsinkovoy rudyi Yubileynogo mestorozhdeniya s ispolzovaniem sochetaniya sulfidrilnykh sobirateley [Selective flotation reagent regime of pyrite copper-zinc ore of Jubileynoe deposit using a combination of sulfhydryl collectors]. *Tsvetnyie metallyi* [Nonferrous metals]. No 2. p. p. 16-20.
12. Golikov A. A., Nagirnyak F. I. (1961) Kataliticheskoe okislenie ksantogenata v vodnom rastvore v prisutstvii sulfidnykh mineralov [Catalytic oxidation of xanthate in an aqueous solution in the presence of sulfide minerals]. *Tsvetnyie metallyi* [Nonferrous metals]. No.4. p.p. 9-11.
13. Ryaboy V. I. (2008) O poverhnostnykh reaktivnykh flotoreagentov s mineralami na osnove ih donorno-aktseptornogo vzaimodeystviya [On the surface reactions of flotation reagents with minerals based on their donor-acceptor interaction]. *Obogashchenie rud* [Ore dressing]. No.6. p.p. 24-30.
14. Abramov A. A. (1978) *Teoreticheskie osnovy optimizatsii selektivnoy flotatsii sulfidnykh rud* [Theoretical bases of optimization of selective flotation of sulphide ores]. Moscow: Nedra. 280 p.