

N. K. TUSSUPBAYEV¹, L. V. SYEMUSHKINA^{1*}, D. K. TURYSBEKOV¹, N. S. BEKTURGANOV²,
A. M. MUKHAMEDILOVA¹

¹*Institute of Metallurgy and Ore Beneficiation, Almaty, Kazakhstan, *syomushkina.lara@mail.ru*

²*Kazakh National Academy of Nature Sciences, Almaty, Kazakhstan*

MODIFIED REAGENTS USING for FLOTATION TAILINGS RECYCLING

Abstract: Research and development of new more selective reagents-collectors for improvement of flotation process efficiency represent one of the main priorities in the development of innovative technologies pertaining to flotation separation of various substances and minerals. The use of collectors' mixtures is being considered as the universal instrument for ensuring necessary proportion in every individual case with respect to the amounts of chemically and physically sorbed collecting reagents on the surface of floatable minerals. Currently hard-dressed, refractory ores and secondary raw materials, which characterized by the low content of valuable components, fine dissemination of mineral assemblages and similar technological properties of minerals constituent are widely involved in the recycling processes. The possibility of processing tailings after flotation beneficiation was studied by using as example tailings of the Zhezkazgan beneficiation plant and the Tishinsk copper ore deposit with application of the modified multifunctional flotation reagents. Modified polyfunctional collector is the mixture of composite airfloat, TC-1000 and butyl xanthate. Reactants ratio is 1:1:3. The advantage of the suggested flotation reagents is that they are composed of two polar groups and have a long hydrocarbon radical. This structure being in the water during flotation process plays a dual role: first, as a collector adsorbing on the mineral surface it produces metal complexes with polar groups in the form of bridges, second, apolar radicals flocculate valuable slimed components, thereby intensifying flotation process. It was shown that flotation of Zhezkazgan tailings with application of the lesser modified reagent amount compared to butyl xanthate has enabled to produce crude copper concentrate with 13.0 % copper content and 80.22 % recovery degree. Compared to the baseline technology copper content in crude concentrate increased by 5.1 %, recovery degree – by 31.4 %. In case of Tishinsk tailings' flotation copper recovery into the collective concentrate increased by 2.14 %, zinc – by 8.64 %, Fe – by 4.56 %, gold – by 5.5 %.

Keywords: flotation tailings, re-grinding, recovery, polyfunctional reagent, flotation, concentrate

Introduction. The importance of carrying out complete and comprehensive development of various deposits as well as ensuring high profitability of processing enterprises, improvement of environmental conditions in the mining regions determine the relevance of scientific investigations related to intensification of methods for valuable components recovery from refractory and secondary raw materials.

In the industrial practice related to sulfides, oxidized minerals of heavy non-ferrous metals, native and precious metals flotation only xanthates, dialkylidithiophosphates and mercaptans are being widely used at present. Only 5-6 types of sulphhydryl collectors are being used for selective recovery from ores of more than 40 mineral of heavy non-ferrous and precious metals, formed by 15 elements, featuring different physical-chemical and flotation properties.

Several new reagents out of multiple combinations with three the most important donor atoms (S, N and O) in the main group of bonds, including several complexing agents, have been tried as the collectors and obtained results have been extensively discussed in numerous books and review papers [1-2].

Large number of organic compounds has been suggested to be used as collectors, but actually not more than 160 compounds are being used in practice. These reagents are being used for selective hydrophobization (lowering wettability level) of the specific

mineral particles' surface, which causes adhesion of mineral particles to gas bubbles. Hydrophobization takes place because of the hydrate film displacement from the surface of mineral. Adhesion of bubbles is caused by the chemisorption (chemical bond formation) or the physical adsorption (van der Waals forces). Depending on the structural characteristics there can be anionic, cationic, amphoteric and non-ionic collectors. Modern practice of using collectors in the process of sulfide ores' flotation in the majority of cases envisages shared use of xanthates and air-floats (anion sulphhydryl collectors). In addition to xanthate, application of airfloats not only provides opportunity for improving quality of the resulting sulphide concentrates because of more selective action of airfloats, but it also increases recovery of metals due to airfloats' ability to ensure efficient flotation of fine particles.

The use of collectors' mixtures represents universal mean for producing the required proportion of chemically and physically sorbed collector amounts on the floatable mineral surface in every specific case.

Currently hard-dressed, refractory ores and man-made raw materials, which are characterized by the low content of valuable components, fine dissemination of mineral assemblages and similar technological properties of constituent minerals are widely involved in the recycling process.

Preparation of old tailings before carrying out

benefication operations plays important role in the achievement of high technological results. Preparatory operations may include re-grinding of tailings, fractionation, de-sliming and washing [3-5].

The purpose of the work is research of possibility of the modified flotoreagents application at technogenic waste beneficiation.

Research Methods. Mineralogical analysis, X-ray analysis (X-ray diffractometer D8 ADVANCE, Germany); X-ray fluorescence analysis (XRF spectrometer with wave dispersion Venus 200 PANalytical B.V. (PANalytical B.V., Netherlands), chemical analysis, flotation (at flotation machines FL-290, FM-1, FM-2 (Russia).

Experimental Part and Results Discussion.

Research work has been done for studying the possibility of processing tailings left after flotation beneficiation at the Zhezkazgan beneficiation plant and flotation tailings of the Tishinsk copper ore deposit with application of multifunctional flotation agents [6-8].

Reagent mixture, collective capacity of which varies depending on pH environmental value, has been selected for working out multifunctional flotation agents. This solution enables selective separation of sulfide minerals with similar physical-chemical properties. Therefore the following initial reagents have been used for carrying out this work: butyl xanthate (BX), thionocarbamate of brand TC-1000 (product from China) and composite airfloat. Composite airfloat has been synthesized from the purified fusel oil and phosphorus sulfide (V).

The advantage of the suggested flotation reagents' utilization is that they are composed of two polar groups and have a long hydrocarbon radical. This structure of flotoreagent being in the water during flotation process plays a dual role: first, as a collector it is adsorbed on the mineral surface; second, apolar radicals flocculate valuable slimed components, thereby intensifying flotation process. Optimal reactants' ratio in the polyfunctional reagent composition was chosen, which resulted in the following composite airfloat formation: thionocarbamate TC-1000 : butyl xanthate sodium = 1:1:3. The mineral composition of Zhezkazgan concentrating factory tailings after flotation enrichment was investigated, by the getting results the main components of the tails were minerals: SiO₂, quartz, CaCO₃, calcite, a plagioclase like albite Na[AlSi₃O₈], an orthoclase K[(Si, Al)₄O₈], muscovite KAl₂[(OH, F)₂AlSi₃O₁₀]. The technological mode for flotation of tailings after flotation enrichment with application of basic flotoreagent – butyl xanthogenate and T-80 frother is worked out. According to chemical analysis results Zhezkazgan tailings contain, %: 0.13

– Cu, 0.01 – Pb, 0.01 – Zn; 66.31 – SiO₂; 2.3 – Fe_{Total}; 11.8 – Al₂O₃; 5.96 – CaO; <0.0003 – Cd; 0.16 – S. Dispersion analysis of tailings has been done along with the study of copper and iron distribution with respect to the grain-size category. Dispersion analysis results are shown in Table 1.

Table 1 – Dispersion analysis results of flotation beneficiation tailings of the Zhezkazgan beneficiation plant

Grain-size category, μm	Yield, %		Content, %		Distribution, %	
	g	%	Cu	Fe	Cu	Fe
-74 +60	82.3	41.15	0.11	4.68	42.26	42.52
-60+50	10.1	5.05	0.64	3.96	30.17	4.41
-50+40	10.5	5.25	0.05	3.6	2.45	4.17
-40+30	14.5	7.25	0.04	3.6	2.71	5.76
-30+20	8.4	4.2	0.046	2.88	1.80	2.67
-20+10	13.8	6.9	0.053	4.68	3.41	7.13
-10+0	60.4	30.2	0.061	5.0	17.2	33.34
Initial tailings	200	100	0.1071	4.53	100	100

Data of Table 1 show that the main part of copper (72.43 %) is contained in the grain-size category of -74+50 μm as well as in the category smaller than 10 μm (17.2 %).

Carried out research work has included development of technological modes for processing flotation tailings of the Zhezkazgan beneficiation plant with the help of basic and multifunctional flotation reagents, as well as refinement of tailings' re-grinding modes and determination of the optimal consumption of reagents. Flotation has been performed with utilization of separate reagents as well as with the different combinations thereof.

Flotation beneficiation scheme of the Zhezkazgan beneficiation plant tailings for crude copper concentrate production is shown in figure. The scheme included re-grinding of initial tails, the main and control flotations, three recleanings of crude copper concentrate.

Results of flotation beneficiation of the Zhezkazgan beneficiation plant tailings with the optimal reagents' consumption are shown in Table 2.

Data of Table 2 show that use of polyfunctional reagent (mixture of composite airfloat, thionocarbamate TS-1000 and butyl xanthate (BX) in the ratio 1:1:3) in flotation process of the Zhezkazgan copper concentrate plant tailings allows to improve process beneficiation results in comparison with the other reagents.

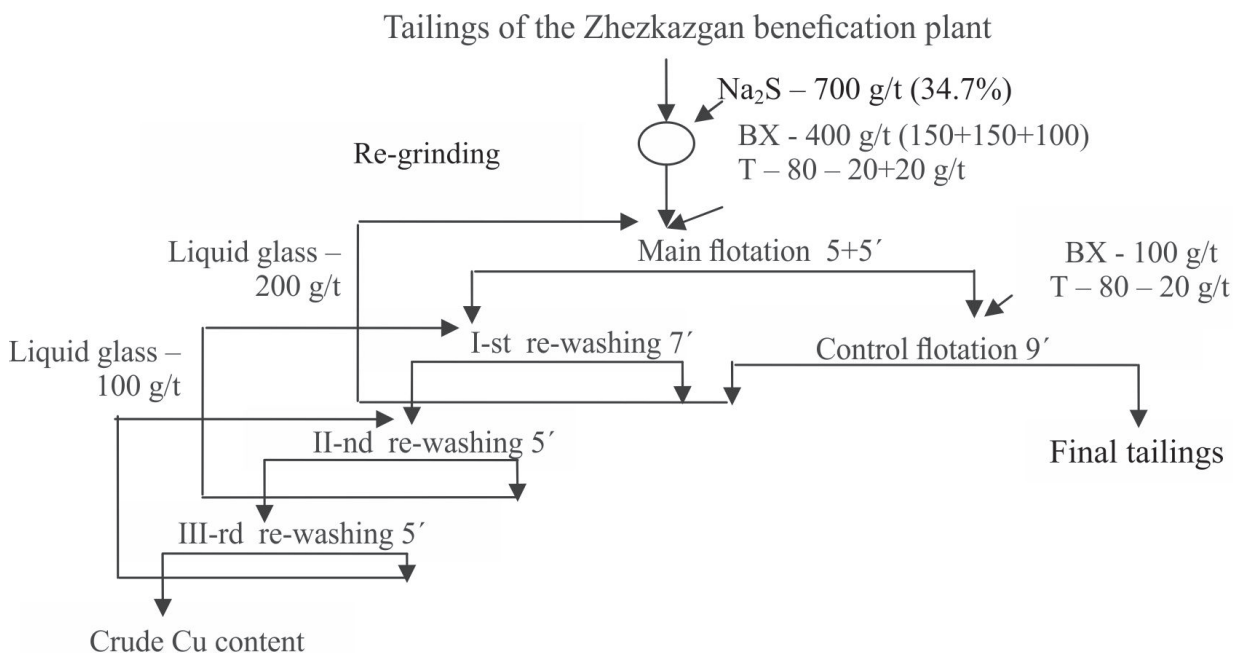


Figure – Scheme of flotation beneficiation of the Zhezkazgan beneficiation plant tailings for crude copper concentrate production

Table 2 – Flotation beneficiation results of the Zhezkazgan copper making plant tailings in case of various reagents' utilization

Name of product	Yield, %	Content, %		Recovery, %		Notes
		Cu	Fe	Cu	Fe	
Crude Cu concentrate	0.6	7.9	10.7	48.82	1.98	BX, 250 g/t
Final tailings	99.4	0.05	3.2	51.18	98.02	
Initial flotation tailings	100	0.097	3.25	100	100	
Crude Cu concentrate	0.62	12.1	10.7	76.65	2.11	BX + thionocarbamate = 3:1, 60 g/t
Final tailings	99.38	0.023	3.1	23.35	97.89	
Initial flotation tailings	100	0.098	3.15	100	100	
Crude Cu concentrate	0.62	13.0	9.6	80.22	1.78	Polyfunctional reagent, 25 g/t
Final tailings	99.38	0.02	3.3	19.78	98.22	
Initial flotation tailings	100	0.100	3.34	100	100	

Crude copper concentrate with 7.9 % copper content and 48.82 % copper recovery degree has been produced under the baseline technology with utilization of butyl xanthate (250 g/t) only. The use of thionocarbamate (60 g/t) alone and in combination with butyl xanthate allows to increase copper content of crude copper concentrate up to 12.1 % and achieve copper recovery degree up to 76.65 %.

The best results with respect to the content and recovery degree of copper obtained by processing Zhezkazgan copper concentrate plant tailings have been achieved with the help of polyfunctional reagent, consumption of which is much lower compared to ba-

sic reagents (25 g/t). Application of this technology has allowed to obtain crude copper concentrate with 13.0 % copper content and 80.22 % recovery degree.

Reagents' utilization mode for flotation of the Tishinsk copper ore deposit tailings with application of modified polyfunctional reagents has been developed.

Chemical analysis shows that investigated tailings' sample contained, %: 0.05 – Cu, 0.06 – Pb, 1.1 – Zn; 52.3 – SiO₂; 2.3 – Fe_{Total}; 8.1 – Al₂O₃, 2.5 – Cao and 8.7 – MgO.

Dispersion analysis of flotation beneficiation tailings of the Tishinsk copper ore deposit has shown that the major part of valuable components, i.e. copper, lead and zinc is contained in 0 - 10 μm fraction.

Flotation scheme included re-grinding of tailings, main and control flotation as well as four re-washing operations of collective copper-lead-zinc concentrate.

Selection of the optimal mode of re-grinding, collector and foaming reagent consumption in the process cycle of collective copper-lead-zinc flotation of the Tishinsk copper ore deposit has been done. Collective copper-lead-zinc concentrate containing, % (recovery degree, %): Cu – 2,5 (61,7); Pb – 2,0 (59,52); Zn – 4,3 (59,41); Fe – 8,3 (40,4); Au – 5,8 г/т (53,41) has been obtained in the process of carrying out optimum re-grinding of tailings up to 75.0 % of -0.040 mm fraction with collector consumption of 150 g/t and foaming agent T-92 consumption of 80 g/t.

Application of modified polyfunctional reagent (the mixture of composite airfloat, thionocarbamate TS-1000 and butyl xanthate in the ratio 1:1:3) allows to increase recovery of valuable components in collective copper-lead-zinc concentrate produced from copper ore beneficiation tailings of the Tishinsk copper ore deposit with reduced consumption of foaming agent T-92 by 25 %, from 80 to 60 g/t. At use of the modified multipurpose agent has allowed to obtain collective copper-lead-zinc concentrate containing, % (recovery degree, %): Cu – 2,6 (63,84); Pb – 2,1 (59,87); Zn – 5,0 (68,05); Fe – 8,7 (44,96); Au – 5,8 г/т (58,91). The recovery of copper has been increased by 2.14 %, zinc – by 8.64 %, iron – by 4.56 %, gold – by 5.5 %.

Conclusion. Thus on the basis of integrated research work the selective modified polyfunctional collector consisting of mixtures of composite airfloats, TC-1000 and butyl xanthate has been chosen. Reactants' ratio was 1:1:3.

Reagent action has been studied on tailings of the Zhezkazgan beneficiation plant and the Tishinsk copper ore deposit.

It has been also shown that in case of Zhezkazgan tailings' flotation with utilization of smaller amount of modified reagent compared to butyl xanthate has allowed to produce crude copper concentrate with 13.0 % copper content and 80.22 % recovery degree. Compared to baseline technology copper content in crude concentrate has increased by 5.1 %, recovery degree – by 31.4 %. In case of Tishinsk tailings flotation copper recovery in the collective concentrate has increased by 2.14 %, zinc – by 8.64 %, iron – by 4.56 %, gold – by 5.5 %.

REFERENCES

- 1 Abramov A.A., Onal G. Requirements of theory and technology to the surface state of minerals to be floated. *X International Mineral Processing Congress: Proceedings of IMPC*, Izmir, Turkey, September 2004. (in Eng.)
- 2 Alan N. Buckley, Gregory A. Hope, Kenneth C. Lee, Eddie A. Petrovic, Ronald Woods Adsorption of O-isopropyl-N-ethyl thionocarbamate on Cu sulfide ore minerals. *Minerals Engineering*. 2014. 69. 120-132 (in Eng)
- 3 Bocharov V.A., Ignatkina V.A., Khachatryan L.S. *Pererabotka piritnyh tehnogennyh produktov* (Processing of pyrite man-made products). *IX Kongress obogatitelej stran SNG: Mater.* (IX Congress of CIS Experts in Materials' Beneficiation: proceedings). Moscow, Russia February 26-28. 2013. 1.122-125. (in Russ.)
- 4 Xumeng Chen, Yongjun Peng, Dee Bradshaw The effect of particle breakage mechanisms during regrinding on the subsequent cleaner flotation. *Minerals Engineering*. 2014. 66–68.157-164 (in Eng).
- 5 Bocharov V.A., Ignatkina V.A. *Racional'nye tehnologii flotatsii trudnoobogatimyykh kolchedannykh rud tsvetnykh metallov* (Rational

flotation technologies of hard-dressed pyritic ores of non-ferrous metals). *Novye tekhnologii obogashcheniya i kompleksnoj pererabotki trudnoobogatimogo prirodnogo i tehnogennogo mineral'nogo syr'ya: Mater. Mezhdunar. Soveshch. Plaksinskie chteniya–2011*. (New technologies of beneficiation and integrated processing of hard-dressed natural and man-made mineral raw materials: Proceedings of International. Conf. Plaksin readings - 2011). – Verkhnyaya Pyshma, Russia September 19-24. 2011. 17-22. (in Russ.).

6 Musina M.M., Shautenov M.R., Tusupbayev N.K., Turysbekov D.K., Syemushkina L.V., Muhamedilova A.M. *Flotatsiya khvostov s primeneniem ehkologicheskii bezopasnykh polifunksional'nykh flotoreagentov* (Flotation of tailings with use of ecology safety polyfunctional flotation reagents). *Vestnik KazNTU = Herald of KazNTU*. 2014. 4. 363-369. (in Russ.).

7 Bekturganov N.S., Tusupbayev N.K., Syemushkina L.V., Turysbekov D.K. Application of multifunctional flotation reagents for processing of man-made raw materials. *16th SGEM Geo Conferences: proceedings*. Albena, Bulgaria. 2016. 1035-1042 (in Eng).

8 Syemushkina L.V., Turysbekov D.K., Tusupbayev N.K., Kotova O.B. *Tekhnologicheskie osnovy pererabotki khvostov flotatsionnogo obogashcheniya s primeneniem kombinirovannykh flotoreagentov* (Technology for recycling flotation tailings by using combined flotation reagents). *Vestnik instituta geologii Komi NTS UrO RAN = The Bulletin of Institute of Geology of Komi Scientific Center of Ural Branch of Russian Academy of Sciences*. 2016. 6. 28-32. (in Russ.).

ЛИТЕРАТУРА

- 1 Abramov A.A., Onal G. Requirements of theory and technology to the surface state of minerals to be floated // *X International Mineral Processing Congress: Proceedings of IMPC – Izmir, Turkey, September, 2004*.
- 2 Alan N. Buckley, Gregory A. Hope, Kenneth C. Lee, Eddie A. Petrovic, Ronald Woods Adsorption of O-isopropyl-N-ethyl thionocarbamate on Cu sulfide ore minerals // *Minerals Engineering*.- 2014.- Vol. 69.- P. 120-132.
- 3 Бочаров В.А., Игнаткина В.А., Хачатрян Л.С. Переработка пиритных техногенных продуктов // IX Конгресс обогатителей стран СНГ: матер. конгр., Москва, Россия, 26-28 февраля 2013. – Т.1. – С. 122-125.
- 4 Xumeng Chen, Yongjun Peng, Dee Bradshaw The effect of particle breakage mechanisms during regrinding on the subsequent cleaner flotation // *Minerals Engineering – 2014.-Vol. 66–68.- P. 157-164*.
- 5 Бочаров В.А., Игнаткина В.А. Рациональные технологии флотации труднообогатимых колчеданных руд цветных металлов // Новые технологии обогащения и комплексной переработки труднообогатимого природного и техногенного минерального сырья: матер. междунар. совещ. (Плаксинские чтения – 2011). – Верхняя Пышма, Россия, 19-24 сентября 2011. – С.17-22.
- 6 Мусина М.М., Шаутонов М.Р., Тусупбаев Н.К., Турысбеков Д.К., Семушкина Л.В., Мухамедилова А. Флотация хвостов с применением экологически безопасных полифункциональных флотореагентов // *Вестник КазНТУ.- 2014.- № 4 (104).- С. 363-369*.
- 7 Bekturganov N.S., Tusupbayev N.K., Syemushkina L.V., Turysbekov D.K. Application of multifunctional flotation reagents for processing of man-made raw materials // *16th SGEM Geo Conferences: proceedings – Albena, Bulgaria, 28 Jun - 7 Jul 2016.- P. 1035-1042*.
- 8 Семушкина Л.В., Турысбеков Д.К., Тусупбаев Н.К., Котова О.Б. Технологические основы переработки хвостов флотационного обогащения с применением комбинированных флотореагентов // *Вестник Института геологии Коми НЦ УрО РАН.- 2016.- № 6.- С.28-32*.

ТҮЙІНДЕМЕ

Пайдалы минералдарды флотациялық байытуда тиімді инновациялық технологияларды өңдеу барысында жаңа, неғұрлым селективті реагент-жыйнағыштарды іздеу және құру бірінші кезектегі міндеттердің бірі болып табылады. Өрбір нақты жағдайда минералдың бойына химиялық және физикалық жолмен сорбцияланатын жыйнағыштардың қажетті ара қатынасты мөлшерін табу жолында жыйнағыштардың қосындысын пайдалану әмбебап құрал болып табылады. Қазіргі уақытта өңдеуге кеңінен қиын байытылатын, қажымайтын кендер мен техногенді шикізаттар тартылып жатыр, ондағы бағалы компоненттер төмен сапалы, минералды кешендер ұсақ сіңген және технологиялық қасиеттері жақын болып табылады. Түрлендірілген полифункционалды реагенттің қолдануымен Жезқазған байыту фабрикасының және Тишин (Қазақстан) кенорнындағы кеннің флотациялық қалдықтарын қайта өңдеу мүмкінділігі қаралған. Түрлендірілген полифункционалды реагент композициялық аэрофлоттың, ТС-1000 және бутилді ксантогенаттың қосындысы болып табылады. Реагенттердің қатынасы 1:1:3 құрайды. Ұсынылған флотореагенттің артықшылығы: құрамында екі полярлы топ және ұзын көмірсутекті радикал бар. Флотациялық процесінде суда мұндай құрылым екі рөл атқарады: біріншіден, минералдың бетіне сорбцияланып полярлы топтармен көпірлер түрінде металлды комплекстер құрады; екіншіден, аполярлы радикалдар шламданған пайдалы компоненттерді флокулаға айналдыра отырып флотация процесін қарқындатады. Жезқазған кенорнындағы кеннің флотациялық қалдықтарын байытуда, бутилды ксантогенатпен салыстырғанда түрлендірілген реагенттің аз шығынымен өңделмеген мыс концентраты алынады, ондағы мыстың үлесі 13,0 %, бөліп алу дәрежесі 80,22 % құрайды. Базалық технологиямен салыстырғанда өңделмеген мыс концентратындағы мыстың үлесі 5,1 %-ға, бөліп алу дәрежесі 31,4 %-ға артады. Тишин кенорнындағы кеннің флотациялық қалдықтарын байытуда бірікті концентраттағы мыстың бөліп алу дәрежесі 2,14 %-ға, мырыштың - 8,64 %-ға, темірдің – 4,56 %-ға, алтынның – 5,5 %-ға артады.

Түйінді сөздер: флотациялық қалдықтар, қайтадан ұнтақтау, бөліп алу, полифункционалды реагент, флотация, концентрат

РЕЗЮМЕ

В настоящее время в переработку широко вовлекаются труднообогатимые, упорные руды и техногенное сырье, которые характеризуются низким содержанием ценных компонентов, тонкой вкрапленностью минеральных комплексов и близкими технологическими свойствами слагающих их минералов. Рассмотрена возможность переработки хвостов флотационного обогащения на примере хвостов Жезказганской фабрики и Тишинского месторождения (Казахстан) с применением модифицированного полифункционального флотореагента. Модифицированный полифункциональный собиратель представляет собой смесь композиционного аэрофлота, ТС-1000 и бутилового ксантогената. Соотношение реагентов составляет 1:1:3. Преимуществом предлагаемого флотореагента является то, что он имеет в своем составе две полярные группы и длинный углеводородный радикал. Такая структура в воде во флотационном процессе играет двойную роль: во-первых, как собиратель, адсорбируясь на поверхности минерала, образует металлокомплексы с полярными группами в виде мостиков, во-вторых, аполярные радикалы флокулируют ошамованные полезные компоненты, тем самым интенсифицируя процесс флотации. Показано, что при флотации хвостов Жезказганской фабрики с применением меньшего, по сравнению с бутиловым ксантогенатом, расхода модифицированного реагента, получается черновой медный концентрат с содержанием меди 13,0 % при извлечении – 80,22 %. По сравнению с базовой технологией содержание меди в черновом концентрате повышается на 5,1 %, извлечение – на 31,4 %. При флотации Тишинских хвостов извлечение меди в коллективный концентрат повышается на 2,14 %, цинка – на 8,64 %, железа – на 4,56 %, золота – на 5,5 %.

Ключевые слова: флотационные хвосты, доизмельчение, извлечение, полифункциональный реагент, флотация, концентрат

Received 26.01.2017.