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On the possibility of processing technogenic flotation raw materials of Kazakhstani deposits with the use of a modified collector

Abstract: The purpose of work - flotation processing of copper-lead-zinc tailings using a modified collector - a mixture of modified butyl xanthate and aeroflot in combination with N-allyl-o-isobutylthionocarbamate. According to the results of X-ray fluorescence analysis in the initial sample of flotation enrichment tailings, the content of lead was 0.048%, copper - 0.03%, zinc - 1.501%, iron - 2.863%. The main part of tailings is represented by rock-forming minerals: quartz, calcite, talc, chrysotile, albite, clinochlore, muscovite, dolomite, and pyrite. The optimal basic reagent scheme of tailings flotation was selected: degree of regrind 78% of -0.040 mm class, sodium butyl xanthate consumption 150 g/t, T-92 frother consumption 80 g/t. Under the selected regime, a collective copper-lead-zinc concentrate was obtained containing 2.0% copper at 67.11% recovery; 1.6% lead at 62.02% recovery; 3.2% zinc at 62.02% recovery; 7.0% iron at 41.67% recovery; 4.1 g/t gold at 54.45% recovery. The reagent scheme of flotation of copper-lead-zinc tailings with the application of a modified collector was tested. Its application allows for increased recovery in the collective copper-lead-zinc concentrate: copper - by 9.63%, lead - by 8.41%, zinc - by 9.2%, iron - by 2.73%, gold - by 3.57%. At the same time the consumption of modified collector, compared to butyl xanthate, is reduced by 33%, and the consumption of basic foaming agent T-92 is reduced by 25%.

Keywords: anthropogenic waste, flotation, modified collector, concentrate.

Introduction

Search and development of new more selective reagent-assemblers to improve the flotation process is one of the priority tasks in the creation of innovative technologies for the flotation separation of substances and minerals. Involvement in the processing of large volumes of hard-to-enrich raw materials requires the use of new technological methods and reagent regimes (Wang et al., 2022; Hornn et al., 2021; Wang & Liu, 2021). Uneven dissemination, fine intergrowth of ore minerals among themselves and with rock minerals, unfavorable ratio of separated minerals considerably complicate obtaining high technological parameters of enrichment (Ignatkina & Bocharov, 2010; Kenzhaliyev, 2019; Semushkina & Narbekova, 2021). The analysis of existing enrichment schemes shows that a significant part of metals in tailings (raw materials of complex composition with low metal content) cannot be effectively extracted using the methods used for primary raw materials. In general, ore dressing tailings are represented by finely groundmass, with the lack of a clear structure, heterogeneity of material composition, mutual sprouting of minerals, variability of physical and chemical properties of mineral surfaces under the influence of oxidation, corrosion, leaching and some other processes (Semushkina et al., 2023). The creation of general principles for selecting compositions of collectors for selective flotation of separated minerals, and the development of reagent regimes based on the use of a combination of collectors of different ionogenicity remains an urgent task (Ryaboy, 2011; Bocharov et al., 2010; Semushkina et al., 2021). The following combinations of sulfhydryl collectors are known: collectors with the same solidophilic group, but with different lengths of the hydrocarbon radical (ethyl and butyl xanthates, etc.); collectors with different solidophilic groups (xanthates and dithiophosphates, dithiophosphates and mercaptobenzothiozoles, etc.); ionic and nonionic collectors (xanthates and dixanthogenides; xanthates and thionocarbamates; dithiophosphates and dialkyl sulfides, etc.) (Ignatkina et al., 2022; Ignatkina et al., 2010; Ignatkina, 2011).

Studies have shown that a selectively acting combination of ionogenic sulfhydryl scavengers should consist of 35% of weak and 65 % of strong scavengers. In practice, the most commonly used combination of weak and strong ionogenic sulfhydryl scavengers is a 1:1 mass ratio. As non-ionogenic components disulfides, thionocarbamates, esters of xanthogenic acids, thioamides, dialkyl sulfides, etc. are used. (Zharolla et al., 2020). There are different points of view on the mechanism of action of the combination of weak and strong collectors, but most agree that the effect of action is associated with the formation of adsorption layer on the surface of the separated minerals. Abramov A.A. formulated the principle of the optimal ratio of chemical and physical forms of sorption of collectors on minerals for successful flotation (Ignatkina, 2016; Turysbekov et al., 2022). Current wastes of enrichment plants and previously formed technogenic mineral formations are promising georesources, which can be effectively developed at the current level of engineering and technology development (Bulaev & Melamud, 2015; Kondratyev et al., 2014).

Hundreds of millions of tons of flotation tailings, which contain significant amounts of non-ferrous and noble metals, are accumulated in the tailings ponds of Kazakhstan enrichment plants processing various ores. In the conditions of significant depletion of balance reserves of ores of Kazakhstan deposits and reduction of their quality, enrichment wastes can be considered as an additional source of metals, despite their lower content of valuable components compared to ore.

Research methods

The following scientific and analytical equipment was used to perform the research: X-ray diffractometer D8 ADVANCE, X-ray fluorescence spectrometer Venus 200 PANalyical B.V., atomic emission spectrometer Optima 2000 DV, electron scanning microscope JEOL JXA-8230, FT-IR spectrometer "Avatar 370". Also, in the process of work technological equipment was used: ball mill 40ML-000PS; flotation machine FML; photometric sedimentometer FSh-6K; disperser T18 ULTRA-TURRAX; eraser for samples MM-1. The objects of research were copper-lead-zinc tailings of Kazakhstani deposit and modified collector. A mixture of modified butyl xanthate and aeroflot in combination with N-allyl-o-isobutyl thionocarbamate was used as a modified collector for efficient processing of flotation dressing tailings. Modified butyl xanthate and aeroflot were obtained based on Kazakhstani raw materials - modified syrup oil, a waste product of alcohol production.

Results and discussion

The research on studying the mineral and granulometric composition of flotation enrichment tailings and development of technological modes of flotation of flotation enrichment tailings with the use of basic flotation agents was carried out.

According to the results of mineralogical analysis, the main mass in the sample of flotation enrichment tailings is: quartz α-SiO_2, calcite $CaCO_3$, talc $Mg_3Si_4O_{10}(OH)_4$, chrysotile $Mg_6Si_4O_{10}(OH)_8$, albite $NaAlSi_3O_8$, muscovite $KAl_2Si_3AlO_{10}(OH)_2$, pyrite FeS_2.

Chemical, spectral, X-ray fluorescence and X-ray phase analyses were done. X-ray phase analysis was performed on a D8 Advance diffractometer (BRUKER), α-Cu emission. The results of X-ray phase analysis are presented in Table 1.

Atomic emission qualitative spectral analysis was carried out, which showed that flotation enrichment tailings contain: Si – very much; Fe - very much; Mg - very much; Ca – much; Al – much; Na – intensive lines; Mn - intensive lines; Ti - intensive lines; Cr - ≥ 0.03 %; Ni - ≥ 0.003 %; Bi - ≤ 0.001 %; Cu - ≤ 0.05 %; Pb - ~ 0.05 %; Zn - > 1.0 %; As – не обнаружен; V - ≥ 0.01 %; La - ~ 0.001 %; Sb - undetected; Ga - ~ 0.001 %; Ag - ~ 0.003 %.

Table 1. Results of X-ray phase analysis of flotation enrichment tailings

Compound Name	Formula	Distribution, %
Quartz, syn	SiO_2	63.2
Albite (heat-treated)	$Na(AlSi_3O_8)$	14.0
Clinochlore	$(MgFe)5Al(Si_3Al)O_{10}(OH)_8$	7.2
Pyrite	FeS_2	3.5
Sphalerite, syn	ZnS	2.9
Muscovite	$KAl_2(AlSi_3)O_{10}(OH)_2$	2.6
Dolomit	$Ca\,Mg(CO_3)_2$	2.4
Magnesium Carbonate	$Mg(CO_3)$	2.4
Calcium Carbonate	$CaCO_3$	1.8
Sodium Silicat Hydrate	$Na_2SiO_3 \cdot 5H_2O$	3.8

The spectrum of the initial tails (Figure 1) was obtained on a FTIR spectrometer "Avatar 370", in the spectral range of 4000-250 cm^{-1} from the preparation as a suspension on vaseline oil in KRS-5 windows. The spectrum of vaseline oil was taken as a comparison spectrum. Experiment attachment: Transmission E.S.P. Composition of flotation enrichment tailings - main content:

Quartz α-SiO_2 – 1166, 1085, 797, 779, 694, 512, 464, 396, 372 cm^{-1}.

Calcite $CaCO_3$ – 1792, 1419, 882п, 713 cm^{-1}.

Sphalerite ZnS – 292 cm^{-1}.

Muscovite $KAl_2[(OH,F)_2|\ AlSi_3O_{10}]$ – 1034 cm^{-1}.

Mineral type Rhipidolith (Prochlorit) – $(Mg, Fe, Al)_3\ [(OH)_2\ |\ Al_{1,2\text{ - }1,5}\ Si_{2,8\text{ - }2,5}O_{10}]\ Mg_3\ (OH)_6$ - 3566, 3426, 983п, 649п, 464 cm^{-1}.

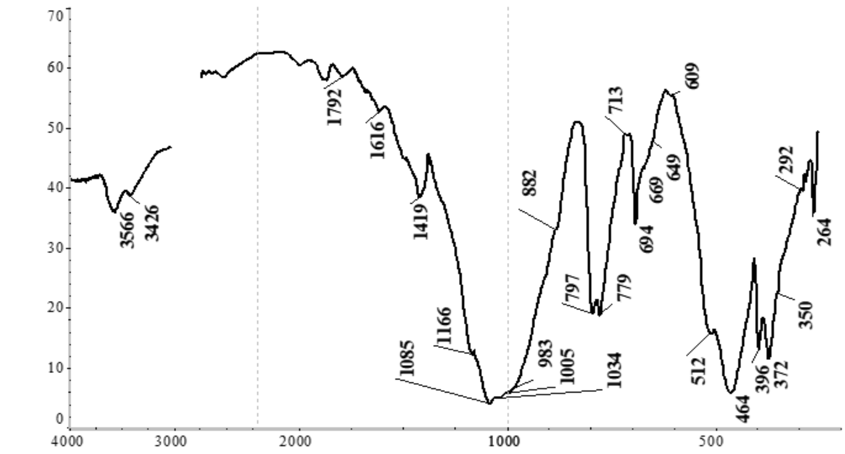
Possibly present:

Pyrite FeS_2 – 350р cm^{-1}.

Albit $Na[AlSi_3O_8]$ – 1166, 1034, 1005, 983п, 649, 609, 464 cm^{-1}.

Anorthite $Ca[Al_2Si_2O_8]$ – 1166, 1085, 669 cm^{-1}.

Transmission



Wave number (cm-1)

Fig. 1. Infrared spectrum of flotation enrichment tailings

X-ray fluorescence analysis of tailings was performed on a Venus 200 PANalyalytical B.V. (PANalytycal B.V., Holland) X-ray fluorescence spectrometer with wave dispersion. The results of the analysis are presented in Table 2.

Table 2. Results of X-ray fluorescence analysis of flotation enrichment tailings

Analyte	Calibration status	Compound formula	Concentration	Unit	Calculation method	Status
O	Calibrated	O	51.548	%	Calculate	BgC; DC
Na	Calibrated	Na	0.163	%	Calculate	BgC; DC; LoR
Mg	Calibrated	Mg	3.343	%	Calculate	BgC; DC
Al	Calibrated	Al	4.104	%	Calculate	BgC; DC
Si	Calibrated	Si	26.859	%	Calculate	BgC; DC
P	Calibrated	P	0.035	%	Calculate	BgC; DC
S	Calibrated	S	1.192	%	Calculate	BgC; DC
Cl	Calibrated	Cl	0.008	%	Calculate	BgC; DC
K	Calibrated	K	0.958	%	Calculate	BgC; DC
Ca	Calibrated	Ca	1.933	%	Calculate	BgC; DC
Ti	Calibrated	Ti	0.170	%	Calculate	BgC; DC
V	Calibrated	V	0.010	%	Calculate	BgC; DC; LoR
Cr	Calibrated	Cr	0.027	%	Calculate	BgC; DC
Mn	Calibrated	Mn	0.122	%	Calculate	BgC; DC
Fe	Calibrated	Fe	2.863	%	Calculate	BgC; DC; LoR
Ni	Calibrated	Ni	0.010	%	Calculate	BgC; DC
Cu	Calibrated	Cu	0.030	%	Calculate	BgC; DC
Zn	Calibrated	Zn	1.501	%	Calculate	BgC; DC
Rb	Calibrated	Rb	0.004	%	Calculate	BgC; DC
Sr	Calibrated	Sr	0.007	%	Calculate	BgC; DC
Zr	Calibrated	Zr	0.005	%	Calculate	BgC; DC
Ba	Calibrated	Ba	0.194	%	Calculate	BgC; DC
Pb	Calibrated	Pb	0.048	%	Calculate	BgC; DC

According to the results of X-ray fluorescence analysis in the initial sample of tailings of flotation enrichment, the content of lead was 0.048 %, copper - 0.03 %, zinc - 1.501 %, iron - 2.863 %. Chemical analysis showed that the sample of the studied tailings contained 0.05 % copper; 0.06 % lead; 1.1 % zinc; 52.3 % SiO_2; 2.3 % total iron; 8.1 % Al_2O_3; 2.5 % CaO; 8.7 % MgO.

Samples of investigated tailings were analyzed on electron-probe microanalyzer JXA-8230 of JEOL company. The results of the microanalysis are shown in Figures 2-5.

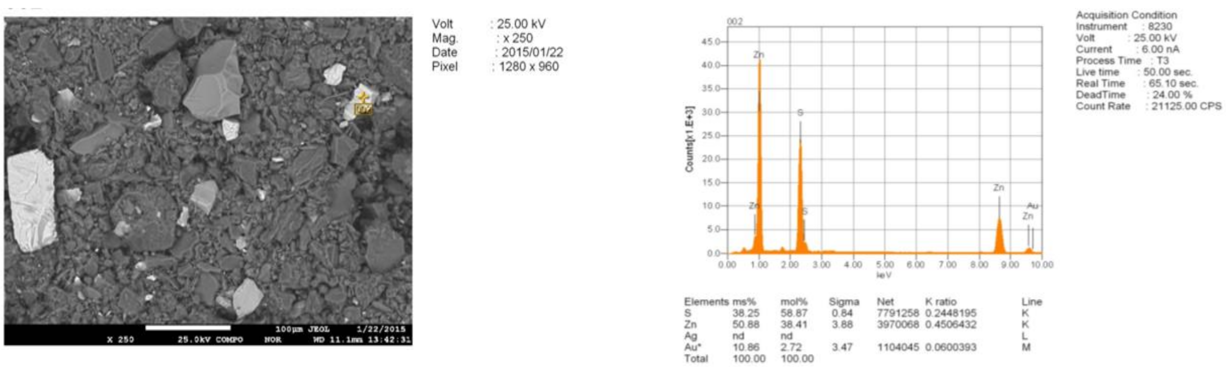
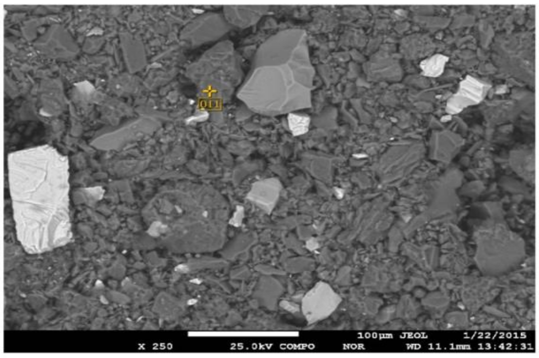
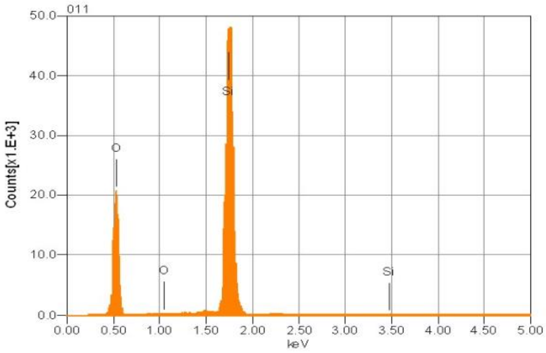


Fig. 2. Analysis of initial tailings of flotation enrichment on electron-probe microanalyzer JXA-8230 by JEOL (zinc minerals)



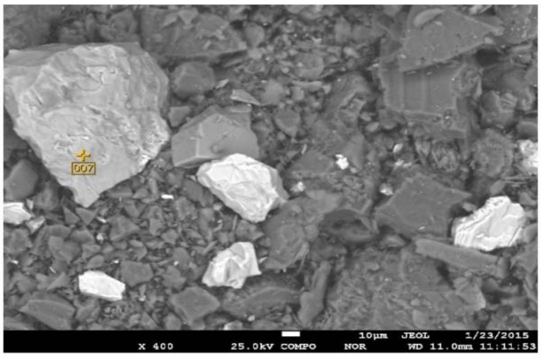
Volt : 25.00 kV
Mag. : x 250
Date : 2015/01/22
Pixel : 1280 x 960



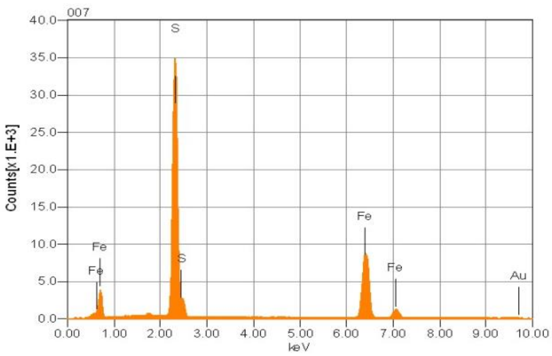
Acquisition Condition
Instrument : 8230
Volt : 25.00 kV
Current : 5.00 nA
Process Time : T3
Live time : 50.00 sec.
Real Time : 60.60 sec.
DeadTime : 18.00 %
Count Rate : 14119.00 CPS

Elements	ms%	mol%	Sigma	Net	K ratio	Line
O	65.92	77.29	1.14	3831840	0.4843100	K
Si	33.98	22.70	0.50	12232193	0.2948830	K
Ag	nd	nd				L
Au*	0.10	0.01	2.99	11350	0.0006188	M
Total	100.00	100.00				

Fig. 3. Analysis of initial tailings of flotation enrichment on electron-probe microanalyzer JXA-8230 by JEOL (silica)



Volt : 25.00 kV
Mag. : x 400
Date : 2015/01/23
Pixel : 1280 x 960



Acquisition Condition
Instrument : 8230
Volt : 25.00 kV
Current : 3.00 nA
Process Time : T3
Live time : 50.00 sec.
Real Time : 61.81 sec.
DeadTime : 19.00 %
Count Rate : 14386.00 CPS

Elements	ms%	mol%	Sigma	Net	K ratio	Line
S	52.33	71.04	0.58	11688632	0.4606162	K
Fe	33.00	25.72	1.43	4169832	0.3403191	K
Ag	nd	nd				L
Au*	14.67	3.24	2.17	1803240	0.1229814	M
Total	100.00	100.00				

Fig. 4. Analysis of initial tailings of flotation enrichment on electron-probe microanalyzer JXA-8230 by JEOL (pyrite)

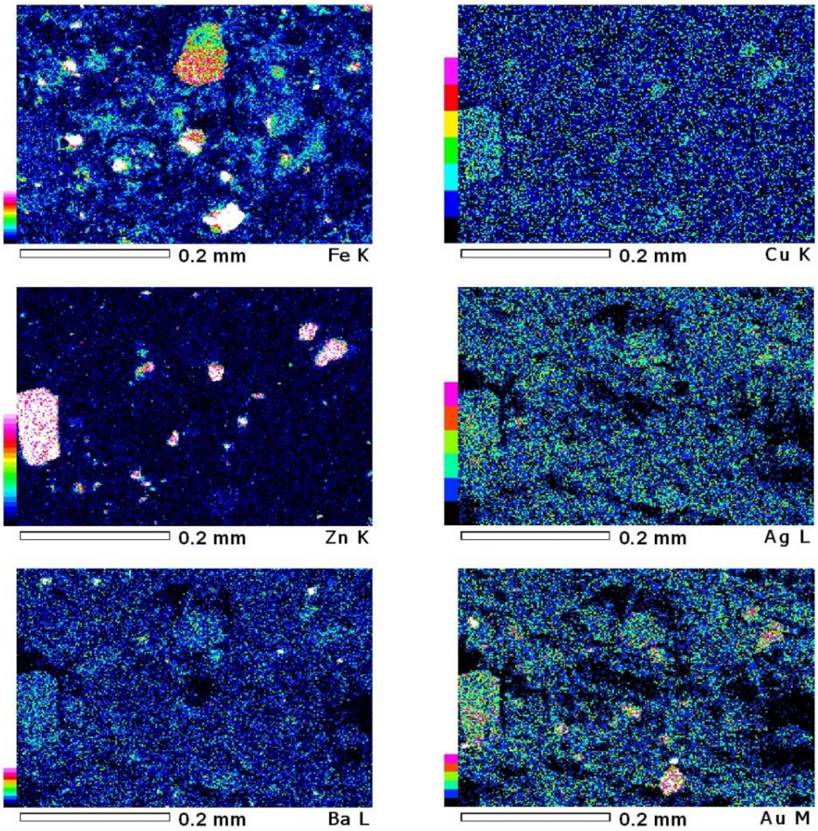


Fig. 5. Distribution of Fe, Cu, Zn, Ag and Au in a sample of flotation tailings sample

To determine the particle size distribution of the initial sample of flotation enrichment tailings, the analysis of variance was carried out, which showed that most of the useful components - copper, lead and zinc are concentrated in the fraction 0-10 microns. The reagent mode of enrichment tailings flotation with the use of basic reagents was tested. The optimum grinding mode, and costs of basic reagents - butyl xanthate and frother - were selected. The scheme of tailings flotation included tailings regrinding, main, control flotation and four recleanings of the collective copper-lead-zinc concentrate. The initial size of flotation tailings by class -0.040 mm was 71.6 %. It follows from the results of studies that additional grinding of flotation tailings up to 78 % of -0.040 mm class allows to increase the degree of extraction of copper, lead, zinc, iron and gold in the froth product by 10-15 %.

The results of studies have shown that the optimal consumption of basic reagents - collector is the consumption of 150 g/t, foaming agent T-92 80 g/t. The use of a modified collector in the flotation cycle of tailings allows to reduce the consumption of frother T-92 by 25 % and increases the recovery of copper, lead, zinc and gold in the collective concentrate. Table 3 shows the results of tailings processing with the modified collector in comparison with the basic mode.

Table 3. Table 3 shows the results of tailings processing with the modified collector in comparison with the basic mode

Name of Products	**Yield, %**	**Content, %, g/t**				**Recovery, %**				**Note**
		Cu	**Pb**	**Zn**	**Au**	**Cu**	**Pb**	**Zn**	**Au**	
Collective concentrate	2.0	2.0	1.6	3.2	4.1	67.1	62.0	62.0	54.45	Basic technology ВКх-150 g/t T-92–80 g/t
Dump tailings	98.0	0.02	0.02	0.04	0.07	32.9	38.0	38.0	45.55	
Initial tails	100.0	0.060	0.052	0.103	0.151	100.0	100.0	100.0	100.0	
Collective concentrate	2.2	2.2	1.8	3.3	4.3	76.7	70.4	71.2	58.02	Modif. collector 100 g/t T-92–60 g/t
Dump tailings	97.8	0.015	0.017	0.03	0.07	23.3	29.6	28.8	41.98	
Initial tails	100.0	0.063	0.056	0.102	0.163	100.0	100.0	100.0	100.0	

The basic technology produced a collective copper-lead-zinc concentrate containing 2.0 % copper at 67.11 % recovery; 1.6 % lead at 62.02 % recovery; 3.2 % zinc at 62.02 % recovery; 7.0 % iron at 41.67 % recovery; and 4.1 g/t gold at 54.45 % recovery.

Flotation using a modified collector produced a collective copper-lead-zinc concentrate containing 2.2 % copper at 76.74 % recovery; 1.8 % lead at 70.43 % recovery; 3.3 % zinc at 71.22 % recovery; 7.1 % iron at 44.4 % recovery; and 4.3 g/t gold at 58.02 % recovery.

Conclusions

The paper presents the results of laboratory studies on flotation processing of copper-lead-zinc tailings using a modified collector. The modified collector is a mixture of modified butyl xanthate and aeroflot in combination with N-allyl-o-isobutylthionocarbamate. Application of the modified collector allows increasing the extraction of useful components in the collective copper-lead-zinc concentrate obtained from the tailings: copper - by 9.63 %, lead - by 8.41 %, zinc - by 9.2 %, iron - by 2.73 %, gold - by 3.57 %. At the same time the consumption of modified collector, in comparison with butyl xanthate, is reduced by 33 % (from 150 to 100 g/t), the consumption of basic frother T-92 is reduced by 25 % (from 80 to 60 g/t).

CRediT author statement: **D.Turysbekov**: Conceptualization; **L.Semushkina**: Methodology, Software, Editing; **Zh.Kaldybayeva**: Data curation, Visualization, Investigation; **N.Tussupbayev**: Supervision, Validation; **S.Narbekova**: Writing draft preparation; **M.Musina:** Reviewing.

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