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On the possibility to process copper-molybdenum ore using a combined flotation reagent

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ABSTRACT The article presents the results of laboratory studies on ore flotation of copper-molybdenum deposits in the East Kazakhstan region of Kazakhstan using a combined reagent. It is required to use new beneficiation methods and flotation reagents to increase the efficiency of flotation of ore minerals to improve the processing of finely disseminated ores. The problem can be solved by using a combination of different collectors. The objective of the research is to increase the recovery of copper and molybdenum during flotation of copper-molybdenum ore using a combined reagent. The studied ore sample contains 0.42% Received: August 04, 2021 copper; 0.009% molybdenum. A combination of sodium butyl xanthate, TS-100 thionocarbamate, and Peer-reviewed: September 20, 2021 reaflot in a ratio, in %: 15: 3: 1, was used as a combined flotation reagent. The combined flotation reagent Accepted: October 15, 2021 was preliminarily passed through an ultrasonic homogenizer JY96-IIN to obtain a reagent microemulsion before flotation. The optimum dispersion time for the combined flotation reagent is 60 seconds. At the same time, 99.4% are microemulsion particles with a particle size of fewer than 3.7 microns. The use of a combined reagent microemulsion increases the extraction of copper into the copper-molybdenum concentrate by 3.69%, and the extraction of molybdenum by 6.05%. The copper content in the coppermolybdenum concentrate increases by 1.26%. The copper content in the flotation tailings decreases from 0.07 to 0.056%. The consumption of the combined reagent is reduced by 15% in comparison with the basic Keywords: flotation, copper-molybdenum ore, flotation reagent, dispersion, concentrate, extraction. Information about authors: Candidate of Engineering Sciences. Leading researcher of the laboratory of flotation reagents and Semushkina Larisa Valerievna beneficiation. Institute of Metallurgy and Ore Beneficiation JSC, Almaty, Kazakhstan ORCID ID: 0000-0001-8925-5250. Email: syomushkina.lara@mail.ru; l.semushkina@satbayev.university Candidate of Engineering Sciences. Leading researcher of the laboratory of flotation reagents and Abdykirova Gulnar Zhanuzakovna beneficiation. Institute of Metallurgy and Ore Beneficiation JSC, Almaty, Kazakhstan ORCID ID: 0000-0001-5956-4730. Email: abdgul@mail.ru; g.abdykirova@satbayev.university Candidate of Engineering Sciences. Leading researcher of the laboratory of flotation reagents and Turysbekov Dulatbek Kadyrbekuly beneficiation. Institute of Metallurgy and Ore Beneficiation JSC, Almaty, Kazakhstan ORCIDID: 0000-0003-0904-1565. Email: dula80@mail.ru; d.turysbekov@satbayev.university Researcher, Laboratory of Flotation Reagents and Beneficiation. Institute of Metallurgy and Ore Beneficiation JSC, Almaty, Kazakhstan ORCID ID: 0000-0002-7325-754X. Email: s.narbekova@mail.ru; Narbekova Sabira Myrzanovna s.narbekova@satbayev.university Junior Researcher, Laboratory of Flotation Reagents and Beneficiation. JSC "Institute of Metallurgy and Kaldybayeva Zhamikhan Beneficiation", Almaty, Kazakhstan. ORCIDID: 0000-0001-5763-9655. Email: arsenti73@mail.ru; Abdildabekovna zh.kaldybaeva@satbayev.university

Introduction

It becomes required to improve the reagent modes of beneficiation of copper-bearing ores, the use of additives and reagent compositions, and the use of modernized equipment, as the deposits are depleted, and the need arises to involve poor, finely disseminated ores in the processing. It is required to use new beneficiation methods and flotation reagents to increase the efficiency of

flotation of ore minerals to improve the processing of finely disseminated ores. Particular difficulties are associated with the processing of the slurry part of the crushed ore, which is usually enriched with non-ferrous, rare, and noble metals [1-5]. Improving the efficiency of flotation can be achieved by using a combination of different collectors [6-10]. The modern practice of using collectors in the flotation of sulfide ores in most cases involves the combined use of xanthate and

aerofloats. The use of aerofloats in addition to xanthogenates enables not only to improve the quality of the obtained sulfide concentrates due to the more selective action of aerofloats, but also to increase the recovery of metals due to the ability of aerofloats to efficiently float fine particles.

Scientists conduct researches to create new dialkyldithiophosphates. The flotation properties of dialkyldithiophosphates and reagents containing them can be significantly influenced by the strong surface-active properties of dialkyldithiophosphates. This was established in the study of surface-active properties in the series of dialkyldithiophosphates with a hydrocarbon chain length C_4 - C_{12} . Dialkyldithiophosphate C_{10} corresponds to the maximum recovery of sulfides [11, 12].

Thus, the problem of finding more effective reagents for the flotation of non-ferrous metals from mineral raw materials is still urgent.

Experimental part

Modern research and analytical equipment were used in the study. Chemical analysis of ore concentration and products performed on an Optima 2000 DV optical emission spectrometer with inductively coupled plasma. Xray fluorescence analysis was performed on a Venus 200 PANalyical B.V spectrometer. We used X-ray phase analysis on a D8 ADVANCE X-ray diffractometer to study the material composition of the ore; spectral analysis on a ThermoNicoletAvatar 370 **FTIR** Spectrometer; electron-probe microanalysis on a JEOL JXA-8230 electron scanning microscope.

The following technological equipment was used: jaw crusher DMD160/100; ball mill 40ML-000PS; flotation machines FML; photometric sedimentometer FSKh-6K; ultrasonic homogenizer JY96-IIN; laser particle analyzer Winner 2000E; mechanical eraser MM-1.

Copper-molybdenum ore of Kazakhstani deposit and combined flotation reagent were used as objects of research. The combined flotation reagent is a mixture of sodium butyl xanthate, thionocarbamate, and reaflot.

The original ore was crushed for research in a laboratory jaw crusher to a size of -2.5 + 0 mm and ground in a laboratory ball mill to 94% of a class of 0.074 mm. A sieve analysis on a set of wire sieves with square holes corresponding to a standard scale was performed to determine the particle size distribution of crushed and milled ore. The weighed

amount of ore was 0.5 kg. Copper and molybdenum content and distribution were determined in each size class. Dispersion analysis was performed on the crushed ore using an FSKh-6K photometric sedimentometer.

Flotation studies were performed on laboratory flotation machines with a volume of 3 chambers; 1.0; 0.5 dm³. The weight of the ore sample was 1 kg. The experiments were performed in open and closed cycles. The flotation scheme included grinding, main flotation, control, and three cleaning operations of the collective copper-molybdenum concentrate. We used 7 weighed portions of ore, 1 kg each in the experiment to achieve a stable distribution of the returned products.

Lime was fed into the grinding process to create a pH of the medium equal to 8.0-9.0; sodium sulfide for the sulfidization of minerals.

main collective copper-molybdenum flotation was performed for 1020 seconds, the control one for 480 seconds, and the following reagents were used in the basic mode as a collector - sodium butyl xanthogenate; foaming agent - T-92. The liquid glass was added to all of the rewashing treatments to depress the minerals in the waste rock. The total consumption of the basic reagents used is: lime (medium regulator) - up to pH 8.0-9.0; sodium sulfide (sulfidizer) - 200 g/t; sodium butyl xanthate (collector) - 180 g/t; liquid glass (depressor) - 150 g/t; T-92 (foaming agent) - 120 g/t. Lime and sodium sulphide were fed into the process of grinding ore into a ball mill. Sodium butyl xanthate and T-92 were fed to the main and control copper-molybdenum flotation. The liquid glass was fed for cleaning collective copper-molybdenum concentrate.

It was fed into the main and control flotation instead of the basic collector of sodium butyl xanthate during flotation processing of ore using a combined flotation reagent. The combined flotation reagent was a mixture of sodium butyl xanthate, TS-100 thionocarbamate, and reaflot in a ratio of 15: 3: 1. The combined flotation reagent before flotation was passed through a JY96-IIN ultrasonic homogenizer to obtain a microemulsion. The optimum particle size of the microemulsion for the best ore flotation was determined on a Winner2000E laser particle analyzer.

The mineral slurry was placed in a flotation chamber after grinding in a ball mill in the presence of sodium sulfide and adjusting the pH (by adding lime) to 8.0-9.0. Sodium butyl xanthate (or combined flotation agent) and foaming agent T-92 were added to it. The mineral slurry was stirred for

60 seconds without air supply at a rotor speed of 1500 rpm. Flotation treatment of the pulp was performed after atmospheric air supply (3.3 dm³/min) according to the applied beneficiation scheme. Liquid glass was added to the first refining of the collective copper-molybdenum concentrate to depress the waste rock.

Results and discussion

The authors of the article have experience in the development and testing of beneficiation schemes using various modified reagents (foaming agents, collectors, depressants) and additional equipment for intensifying flotation processes. A modified foaming agent (MFA) has been developed, used in the form of a microemulsion obtained in a water-air microemulsion generator. The optimum composition of MFA particles was selected on the PhotocorCompact particle size analyzer: the average particle size of microbubbles is 38 microns, the content (fraction) of these particles is 65.8%. In this case, MFA molecules become compact due to intramolecular interactions, due to which they are more efficiently fixed on the surface of small particles of useful components and improve combined microflotation.

The results of experimental studies of collectors from the class of dialkyldithiophosphates (aerofloat) show that their combined use with xanthogenates in many cases provides an increase in metal recovery by 2-3% [13, 14]. The most effective flotation of minerals that do not have natural hydrophobicity is observed in the optimal ratio.

Mineralogical analysis shows that copper minerals in the ore under study are represented mainly by chalcopyrite, chalcocyte and covellite are present in smaller amounts. The main molybdenum mineral is molybdenite. The ore contains pyrite, magnetite, and, to a lesser extent, hematite and ilmenite. In addition, the ore contains a small amount of rutile, galena, sphalerite. The results of the mineralogical analysis are presented in Table 1.

Chalcopyrite exists independently mainly in the form of xenomorphic grains or is associated with pyrite and is unevenly disseminated in vein minerals, sometimes located in the form of veins. Dispersed chalcopyrite grain size varies from 0.001 to 1 mm. Chalcopyrite grain size in veins and nests is generally more than 0.01 mm. Molybdenite is mainly disseminated in quartz in the form of lamellar single crystals or their aggregates. It is

found in calcite, quartz-calcite, and quartz veins. This mineral also forms nests and placers in zones of alteration with potash feldspar.

Table 1 - Results of mineralogical analysis of the initial sample of copper-molybdenum ore

Mineral name	Content, %	
Chalcopyrite	1.05	
Covellin	0.01	
Kholkozin	0.01	
Pyrite	0.4	
Molybdenite	0.014	
Sphalerite	0.04	
Galena	0.016	
Magnetite	2.1	
Hematite	0.1	
Ilmenite	0.2	
Rutile	0.2	
Ti-Fe rutile	0.1	
Quartz	20.6	
Sodium feldspar	26.0	
Calcium Sodium Feldspar	16.0	
Potassium feldspar	7.0	
Potassium microplagioclase	3.0	
Chromite	13.0	
Sericite	4.0	
Biotite	2.0	
Epidote	2.0	
Calcite	1.4	
Titanite	0.6	
Apatite, wollastonite, and others	0.16	

Rock-forming minerals are represented by sodium feldspar, quartz, calcium-sodium feldspar, chlorite, and, to a lesser extent, potassium feldspar, sericite, potassium microplagioclase are present. In addition, there is a small amount of biotite, epidote, calcite, wollastonite, titanite, and apatite.

The studied sample of copper-molybdenum ore contains 0.42% Cu; 0.009% Mo; 0.55% S; 5.1% Fe; 0.012% Pb; 0.025% Zn; 0.001% As; 0.02 g/t Au; 2.1 g/t Ag; 2,92 % K_2O ; 2,93 % Na_2O ; 4,8 % CaO; 14,8 % Al_2O_3 ; 61,5 % SiO_2 ; 2,8 % MgO according to the results of chemical analysis.

Phase analysis of initial ore for copper and molybdenum is performed. The results of the analysis showed that the content of primary copper sulfides (chalcopyrite $CuFeS_2$) in the ore is 95.5%; secondary copper sulfides (chalcocite Cu_2S , covellite CuS) - 2.1%; in the form of copper oxides - 2.4%. The content of molybdenum in the original ore in the sulfide form (molybdenite MoS_2) is 96%; in oxidized form - 4.0%.

An X-ray phase analysis of an ore sample was performed. The diaphragms of the samples were made on a D8 Advance apparatus (Bruker), α -Cu, tube voltage 40/40. The processing of the obtained data of diffraction patterns and the calculation of interplanar distances were performed using the EVA software. The results of the X-ray phase analysis are presented in Table 2.

Table 2 - Results of X-ray phase analysis of the initial sample of copper-molybdenum ore

Compound Name, Formula	S-Q
Quartz, syn SiO ₂	35.1
Albite, calcian, ordered,	
(Na,Ca)Al(Si,Al)₃O ₈	19.7
Clinochlore-2MIIb,	
Mg ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈	14.0
Anorthite, sodian, intermediate,	
(Ca, Na)(Si, Al) ₄ O ₈	13.9
Glagolevite,	
$NaMg_6(Si_3AI)O_{10}(OH,O)_8\cdot H_2O$	4.4
Graphite, syn, C	3.0
Ferrierite,	
(Na,K,Mg) ₂ (Si,Al) ₁₈ O ₃₆ ·9H ₂ O	2.9
Nepheline, potassian, syn, (K,	
Na)AlSiO4	2.4
Illite-2M1 (NR),	
(K,H ₃ O)Al ₂ Si ₃ AlO ₁₀ (OH) ₂	2.3
Muscovite-1M, syn,	
KAl ₂ Si ₃ AlO ₁₀ (OH) ₂	2.0

X-ray phase analysis showed that the main rock-forming minerals in the ore are quartz, albite, clinochlore, etc. X-ray fluorescence analysis of the original ore was performed on a Venus 200 PANalyical B.V. (PANalytycal B.V., Holland). The analysis showed that the main valuable component in the original ore sample is copper, the content of which is 0.462%. The bulk is oxygen - 49.958%, silicon - 23.856%, aluminum - 7.27%, iron - 3.975%, calcium - 2.683%.

A sample of the original ore was analyzed on a JXA-8230 electron probe microanalyzer from JEOL. Polished sections were scanned with fixation of ore and rock-forming minerals with the determination of their composition (Figure 1).

Microscopic examination showed that copper minerals account for about one percent and are represented by chalcopyrite. The sizes of ore minerals range from thousandths to 0.04-0.07 mm in cross-section. They are found in the form of free grains, but more often in the form of inclusions in nonmetallic minerals.

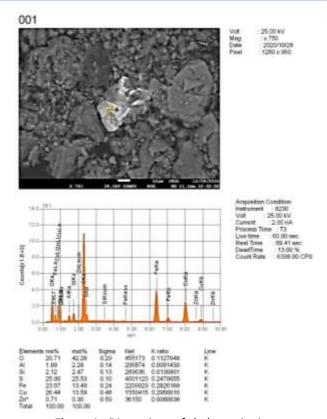


Figure 1 - Dispersions of chalcopyrite in quartz

The granulometric composition of the crushed ore has been determined. The ore was crushed on a laboratory jaw crusher to a size of -2.5 + 0 mm. Further, the ore was ground in a ball mill to a size of 95% of the class -0.071 mm. A set of wire sieves with square holes corresponding to the standard scale was used for sieving. The content and distribution of copper and molybdenum were determined in each size class. The data are presented in Table 3. It was shown that most of the copper and molybdenum in this grinding (75-77%) is distributed in the +50 μm and -20 μm classes. The size class of +50 μm contains 29.08 % copper and 37.93 % molybdenum; the -20 μm size class contains 44.9 % copper and 37.7 % molybdenum.

Table 3 - Granulometric composition and distribution of copper and molybdenum by size classes in crushed ore

Size class,	Outp ut %	Content, %		Distribution, %	
microns		Cu	Мо	Cu	Мо
+71	19.0	0.39	0.015	19.5	28.3
-71+50	12.1	0.3	0.008	9.58	9.63
-50+40	11.9	0.37	0.01	11.6	11.8
-40+30	2.93	0.44	0.01	3.40	2.92
-30+20	10.7	0.39	0.009	11.0	9.58
-20+10	23.6	0.41	0.011	25.6	25.9
-10+0	19.7	0.37	0.006	19.3	11.8
Initial ore	100	0.38	0.010	100	100

Dispersion analysis of crushed ore was performed an FSKh-6K photometric sedimentometer, which is designed to measure the particle size distribution of powders suspensions with a particle size of fewer than 300 microns.

The results of the dispersion analysis of crushed copper-molybdenum ore are shown in Figure 2.

Ore was crushed to a flotation size of 92% of class -0.074 mm for analysis of variance. The results of the dispersion analysis show that the largest part of the initial sample of crushed ore is the size classes of 15-20 microns and 60-70 microns.

The following parameters of flotation of copper-molybdenum ore were worked out: degree of grinding of ore, consumption of sodium butyl xanthate, consumption of foaming agent T-92.

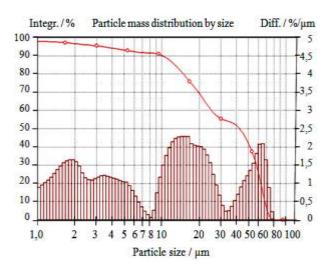


Figure 2 - Dispersion analysis of a sample of crushed copper-molybdenum ore at FSKh-6K

Optimal conditions for flotation are: grinding of 94% ore of class -0.074 mm, Na_2S - 200 g/t; pH 8-9; consumption of butyl xanthate in bulk flotation 160 g/t; T-92 90 g/t; liquid glass in the cleaning of collective copper-molybdenum concentrate 150 g/t. A collective copper-molybdenum concentrate was obtained, in the optimal basic mode, in an open cycle, with a copper content of 16.87% at 76.35% recovery and with a molybdenum content of 0.42% at 78.82% recovery.

The reagent mode of flotation of copper-molybdenum ore with the use of a combined reagent, which is a mixture of sodium butyl xanthate, thionocarbamate, and reaflot in the ratio, in %: 15: 3: 1, has been worked out. Microemulsion of combined flotation agent obtained in JY96-IIN ultrasonic homogenizer allows to improve hydrophobization of slurry particles of copper and

molybdenum minerals. The bubbles of the foaming agent in this case are better fixed on the surface of the floating minerals, which leads to an increase in the technological parameters of floation.

The optimal dispersion time and particle size of the combined reagent microemulsion were selected using a Winner 2000E laser particle analyzer. Figure 3 shows the results of measuring the emulsion particles of the combined reagent. The optimal dispersion time for the combined reagent solution with a concentration corresponding to the flow rate in flotation is 1 min. At the same time, 99.4% are particles with a particle size of fewer than 3.7 microns.

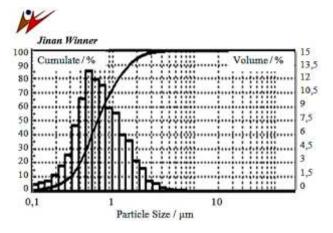


Figure 3 - Particle distribution of the combined reagent obtained on Winner 2000E

Laboratory studies on flotation concentration of ore from a copper-molybdenum deposit in the East Kazakhstan region of Kazakhstan in a closed cycle with the use of a combined flotation reagent in comparison with the basic regime were performed. The results of the flotation of the collective copper-molybdenum cycle are shown in Figure 4.

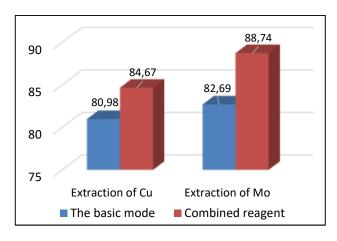


Figure 4 - Results of collective flotation of coppermolybdenum ore in a closed cycle

The presented data show that the use of dispersed microemulsion of combined reagent increases, compared with the basic mode, extraction of copper in the collective coppermolybdenum concentrate by 3.69%, extraction of molybdenum by 6.05%. The copper content in the copper-molybdenum concentrate increases by 1.26%, from 16.8 to 18.06%. The copper content in the flotation tailings decreases from 0.07 to 0.056%. At the same time, the consumption of the combined reagent is 15% less than sodium butyl xanthate.

Thus, the research results show that the use of the combined reagent is promising for the processing of copper-molybdenum ores.

Conclusions

The effect of the combined flotation reagent on the ore flotation of the copper-molybdenum deposit in the East Kazakhstan region of Kazakhstan has been studied. The combined reagent is a mixture of sodium butyl xanthate, thionocarbamate, and reaflot in a ratio, in %: 15: 3: 1. The combined reagent was supplied to the flotation in the form of a microemulsion obtained on an ultrasonic homogenizer JY96-IIN.

The optimal dispersion time of the combined flotation reagent is 60 sec. At the same time, 99.4% are microemulsion particles with a particle size of fewer than 3.7 microns.

Copper-molybdenum concentrate with copper content of 16.8%, molybdenum 0.40%, and recovery of 80.98% and 82.69%, respectively, was obtained in the optimum basic closed-cycle mode. The use of a microemulsion of a combined reagent increases the extraction of copper into the coppermolybdenum concentrate by 3.69%, the extraction of molybdenum by 6.05%. The copper content in the copper-molybdenum concentrate increases by 1.26%. The copper content in flotation tailings decreases from 0.07 to 0.056%. The consumption of the combined reagent, in comparison with the basic butyl xanthate, is reduced by 15%.

Conflict of interests. The correspondent author declares on behalf of all the authors that there is no conflict of interest.

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Құрамдастырылған флотореагентті қолдана отырып мыс-молибден кенін қайта өңдеу мүмкіндігі туралы

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ТҮЙІНДЕМЕ

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Мақалада құрамдастырылған реагентті қолдана отырып, Шығыс Қазақстан кенорнының мысмолибден кенін флотациялау бойынша зертханалық зерттеулердің нәтижелері баяндалған. Ұсақ сеппелі кендерді өңдеу үшін кен минералдарын флотациялаудың тиімділігін арттыруға мүмкіндік беретін байытудың жаңа тәсілдерін және жаңа флотациялық реагенттерді қолдану қажет. Бұл проблеманы әртүрлі жинағыштардың үйлесімді қоспасын қолдану арқылы шешуге болады. Зерттеудің мақсаты - құрамдастырылған реагентті қолдана отырып мыс-молибден кенін флотациялауда мыс пен молибденді бөліп алу дөрежесін арттыру. Зерттелген кен үлгісінде мыстың үлесі 0,42%; молибденнің үлесі 0,009% құрайды. Құрамдастырылған флотореагент ретінде натрий бутил ксантогенатының, ТС-100 тионокарбаматтың және реафлоттың 15: 3: 1 қатынасындағы қоспасы қолданылды. Флотациялаудың алдында реагенттің микроэмульсиясын алу үшін құрамдастырылған реагент JY96-IIN маркалы ультрадыбыстық гомогенизатор арқылы өткізілді. Құрамдастырылған флотациялық реагентті оңтайлы ыдырату (диспергациялау) уақыты

	60 секунд. Бұл жағдайда микроэмульсия бөлшектерінің 99,4%-ның ірілігі 3,7 мкм аспайды. Құрамдастырылған реагенттің микроэмульсиясын қолдану мыс-молибден концентратына мысты бөліп алу дәрежесін 3,69%-ға, молибденді - 6,05%-ға арттырады. Мыс-молибден концентратындағы мыстың үлесі 1,26% -ға артады. Флотациялық қалдықтағы мыстың үлесі 0,07-ден 0,056%-ға дейін төмендейді. Құрамдастырылған реагенттің шығыны базалық бутил ксантогенатымен салыстырғанда 15%-ға төмендейді. Түйін сөздер: флотация, мыс-молибден кені, флотациялық реагент, ыдырату (диспергациялау), концентрат, бөліп алу.
	Авторлар туралы ақпарат: Техника ғылымдарының кандидаты, Флотациялық реагенттер және кен байыту
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О возможности переработки медно-молибденовой руды с применением комбинированного флотореагента

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АННОТАЦИЯ

В статье представлены результаты лабораторных исследований по флотации руды медномолибденового месторождения Восточно-Казахстанской области Казахстана с применением комбинированного реагента. Для повышения эффективности переработки тонковкрапленных руд необходимо применение новых способов обогащения, флотационных реагентов, позволяющих повысить эффективность флотации рудных минералов. Решение проблемы может быть достигнуто применением сочетания различных собирателей. Целью исследований является повышение извлечения меди и молибдена при флотацции медно-молибденовой руды с применением комбинированного реагента. В исследуемой пробе руды содержится 0,42 % меди; 0,009 % молибдена. В качестве комбинированного флотореагента применена комбинация бутилового ксантогената натрия, тионокарбамата ТС-100 и реафлота в соотношении: 15:3:1. Комбинированный флотореагент предварительно перед флотацией для получения микроэмульсии реагента пропускали через ультразвуковой гомогенизатор JY96-IIN. Оптимальное время диспергирования комбинированного флотационного реагента составляет 60 сек. При этом 99,4 % составляют частицы микроэмульсии крупностью менее 3,7 мкм. Применение микроэмульсии комбинированного реагента повышает извлечение меди в медно-молибденовый концентрат на 3,69 %, извлечение молибдена на 6,05 %. Содержание меди в медно-молибденовом концентрате повышается на 1,26 %. Содержание меди в хвостах флотации уменьшается с 0,07 до 0,056 %. Расход комбинированного реагента, по сравнению с базовым бутиловым ксантогенатом уменьшается на 15 %.

Ключевые слова: флотация, медно-молибденовая руда, флотореагент, диспергация, концентрат, извлечение.

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