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Research Article

RESEARCH OF NEW COLLECTING AGENTS INCREASING TECHNOLOGICAL INDICATORS OF COPPER-MOLYBDENUM ORE ENRICHMENT

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ABSTRACT
The article discusses the results of a study of new collecting agents that increase the technological parameters of enrichment of copper-molybdenum ores of the Kalmakyr deposit (Uzbekistan).
The possibility of intensifying ore flotation by improving reagent modes, introducing new reagents, and others is shown. A brief description of the material composition of the copper-molybdenum ores of the Kalmakyr deposit is given. The results of comparative flotation experiments using a traditional collecting agent of potassium butyl xanthate (PBX) and new reagents are presented. The main part of the research is related to the study of the possibility of partial or complete replacement of potassium butyl xanthate with reagents obtained on the basis of local raw materials (shale oil (SO), SD-1, and PB-1) to assess the effectiveness of the enrichment process with verification using flotation tests. New collecting agents have been shown to exhibit good flotation ability. The use of these reagents contributes to the extraction of copper in the concentrate of the main flotation from 88.2 to 93.3%, and molybdenum - from 53.2 to 83.7%. The results for copper are not only comparable to the results of the basic regime, but also for the degree of copper extraction in the concentrate of the main flotation, being higher 17.7-22.9%. Comparable results are indicated both for the extraction of molybdenum, and in the case of using shale oil and PB-1, molybdenum extraction is higher 14.0-26.6%. A flotation of copper-molybdenum ores of the Kalmakyr deposit with an effective increase in the extraction of copper and molybdenum into concentrate using shale resin (shale oil reagent) as a collecting agent has been proposed. So, when using potassium butyl xanthate and shale oil reagents, at a flow rate of potassium butyl xanthate -10 g/t and shale oil - 20 g/t in the main flotation, a rough concentrate was obtained with a yield of 10.8%, containing 5.23% Cu and 0.028% Mo, with their extraction making up 93.3 and 83.7%, which is 22.9 and 26.6% higher than with a single potassium butyl xanthate, respectively. When using shale oil reagent separately, at a flow rate of 40 g/t in the main flotation, a rough concentrate was obtained with a yield of 4.4%, containing 11.32% Cu and 0.052% Mo, with their recovery of 91.8 and 73.9%, which 21.3 and 16.9% higher than with a single potassium butyl xanthate, respectively. Laboratory studies indicate that shale oil reagent can be used as a collecting agent, replacing expensive imported analogues.

Keywords: *Flotation, Concentration, Collecting Agent, Copper-Molybdenum Ores, Kalmakyr Deposit, Shale Oil*

INTRODUCTION
One of the main trends in copper production is to increase the complexity of the use of raw materials and the efficiency of its processing using new collecting agents.
The main copper raw material base and a significant proportion of molybdenum are copper-molybdenum porphyry ores (Abramov, 2005). Porphyry deposits account for 50-60% of world copper production and more than 95% of world molybdenum production. Also, these ores are one of the main sources not only of Cu and Mo, but also of Au, Ag, Sn with accompanied Re, W, In, Pt, Pd, and Se (Bukhanova, 2012; Portnov *et al.*, 2015).
The main method of copper-molybdenum ores enrichment is flotation to obtain a collective copper-molybdenum concentrate followed by its separation into copper and molybdenum concentrates (Andrzej

and Bozena, 2016; Avdokhin, 2006; Abramov, 2008). The collective flotation cycle of sulfide copper-molybdenum ores is mainly carried out using sulfhydryl collectors for sulfide minerals: xanthates, dixantogenides, dithiophosphates, dithiocarbamates, which ensure efficient extraction of copper and molybdenum into a bulk concentrate (Polkin *et al.*, 1983; Abramov, 1984). In practice, as a rule, at least two collecting agents are used (a combination of a sulfhydryl collector with apolar (non-polar oil) oil, ethyl xanthate with amyl oil, etc.) (Shubov *et al.*, 1990).

The task of increasing the degree of valuable components extraction from copper-molybdenum ores into concentrate using new reagents from local raw materials is very urgent. Currently, most of the collecting agents used in the flotation process is imported (Alimov and Umarova, 2010). Therefore, the introduction of new collecting agents and the study of the action mechanism of these collecting agents, as well as their use on an industrial scale, will make it possible to use more efficient and economically feasible technologies for processing the mineral resource base available in the republic.

Laboratory tests of new local collecting agents - shale oil, PB-1, SD-1 during ore flotation of the Kalmakyr deposit and comparison of the results with the traditional collecting agents - butyl potassium xanthogenate (potassium butyl xanthate) were carried out.

MATERIALS AND METHODS

Due to the complexity of the flotation process and the influence for its efficiency of a large number of factors (Bradshaw and *et al.,* 1998) that impede the theoretical analysis of its behavior, the reliable information about this process can be obtained experimentally by conducting flotation tests.

When flotation concentration of copper-molybdenum ores at the processing plants of JSC «Almalyk Mining-and-Metallurgical Combine», the imported reagents (butyl potassium xanthate, 442F, spindle oil) are used as collecting agents (Turakulov and *et al.*, 2019).

For the partial or complete replacement of imported reagents, new collecting agents obtained from local raw materials were tested.

PB-1 is obtained when processing wastes from the Tashvinzavod (fusel-oils) by sulfuric acid with a small amount of catalyst. It is a viscous dark brown liquid with a fragrant odor.

SD-1 is obtained by processing wastes from the Navoi-Azot enterprise with added polyacrylamide, etc.

Shale oil (SO) - is obtained by pyrolysis (thermal decomposition of a material without oxygen) of oil shale, at temperatures of 500-550ºC. Shale oil is the liquid phase of pyrolysis, it has a complex composition. It consists of paraffins, olefins, diolefins, naphthenes, cycloolefins, mono- and bicyclic, as well as polycyclic, aromatic compounds - acids, phenols, ketones, alcohols, ethers; sulfur compounds - mercaptans, sulfides, thiophenes, thiophanes, disulfides and others; nitrogenous compounds - pyridines, quinolines, hydropyridines (Alimov and Borminsky, 2010). The average group composition of shale oil consists of 12.73% paraffins, 3.06% naphthenes, 6.8% olefins, 51.78% aromatic compounds, 23.47% thiophenes, etc. (Alimov and Khoshimov, 2018).

An important source for the production of the widest range of flotation reagents in Uzbekistan can be oil shale of bituminous shale (Alimov and Borminsky, 2010). In the coming years the corresponding production on the basis of oil shale of the Sangruntau deposit is planned to be launched (Isokov and et al. 2015).

Collectors are a large group of organic reagents represented by individual compounds or technical products, which are very diverse in their composition and structure (Tinashe and *et al.,* 2017). These reagents are used to selectively hydrophobize the surface of particles of certain minerals in a flotation pulp and to extract them into a foam product (concentrate) by sticking to air bubbles. Collectors also contribute to a decrease in the wettability of mineral particles by water and their stronger attachment to air bubbles (Andrew and Odair, 2018; Wills and Finch, 2015).

In the course of testing, the traditional and new collecting reagents synthesized in the laboratory of the "Institute of Mineral Resources" State Enterprise and several laboratory installations and methods, which are described below, were used.

The main criteria for the technological evaluation of copper-molybdenum ores enrichment are the features of their material composition, the nature and proportions of the host minerals, the degree of oxidation of the ore, etc.; for their determination the chemical and physicochemical research methods are used: chemical, X-ray fluorescence, mineralogical analysis methods for studying the composition of ore and products of flotation concentration.

Ore grinding was carried out in a laboratory of 40ML mark ball mill with a solid: liquid ratio of balls = 1: 0.75: 8. For ore flotation, a laboratory flotation machine of 237-FLA mark with a chamber capacity of 3.0 l was used. The results of enrichment experiments were evaluated according to chemical analysis for copper and molybdenum using an atomic absorption spectrometer of "Perkin-Elmer" company.

RESULTS AND DISCUSSION

In the course of study of the material composition of a sample of copper-molybdenum ores of the Kalmakyr deposit, it was found that:

- according to the results of chemical analysis, the ore contains, %: SiO_2 - 59.22; Fe_2O_3 - 5.37; FeO - 3.09; TiO_2 - 0.4; MnO - 0.14; Al_2O_3 - 13.26; CaO - 1.68; MgO - 3.2; K2O - 4.74; Na2O - 0.32; shale oil. – 2.09; $S_{sulfide}$. – 1.80; SO_3 - 0.72; CO_2 - 2.75; P_2O_5 - 0.3; ±H_2O - 0.98; cu-0.5; Pb - 0.04; Zn - 0.05; as - 0.02; Mo-0.0055; AU - 0.6; AG - 6.94; Ignition loss - 10.6. According to the phase analysis data, 97.2% of copper in the ore sample is represented by sulfides.
- rock-forming minerals in ore are mainly represented by feldspars, mica, amphiboles, pyroxenes and quartz.
- the main ore minerals in the ore are represented by chalcopyrite, molybdenite, and pyrite. Minerals such as hematite, pyrrhotite, marcasite, galena, sphalerite, bornite, covelin, chalcosine are present in very small quantities and are not of practical interest. The main industrially valuable components of ores are copper and molybdenum. Gold and silver should be referred to associated components. The main industrially valuable copper mineral is chalcopyrite; it forms an uneven, diffuse impregnation in diorites, syenito-diorites, granodiorite-porphyries, quartz, and quartz-calcite veins intersecting them. The overwhelming mass of chalcopyrite 97% of the total number of grains and 83% of the total mineral volume has sizes from 0.01 mm to 0.2 mm.
- gold in chalcopyrites is in a native state and in the form of tellurides and makes up about 22 g/t, silver 65 g/t. According to available data, chalcopyrite contains less than a half of all gold. The bulk of gold is apparently contained in pyrite and partially in vein quartz.
- molybdenum is represented mainly by molybdenite. The content of the latter in ores is utterly low. The mineral is not evenly distributed in the sample material; it is found in the form of individual flakes, the size of which does not exceed the first tenths of a millimeter. According to the results of spectral analyzes, the most interesting impurity elements in molybdenite are copper, silver, lead, arsenic, and in some nickel and chromium. According to the quantitative determination of rare elements, the high content of rhenium, selenium, and tellurium in molybdenites is of particular interest. The selenium content in molybdenites is very high (140 g/t). The tellurium content is lower - 40 g/t, rhenium is about 1000 g/t.
- pyrite is the most common sulfide in the ore. The mineral gives a rather thin impregnation of irregularly shaped grains. The size of selection does not exceed 1 mm on average. Pyrite gives close intergrowths with all ore minerals, carries their thin inclusions. Pyrites contain gold on average of about 3.5 g/t, and the amount of silver varies from 3 to 90 g/t, averaging about 60 g/t, and bismuth is 50 g/t. Despite the fact that the gold content in pyrite is 6 times lower than in chalcopyrite, at least half of the total mass of this element is apparently associated with pyrite, because the concentration of the latter is 5-8 times higher than chalcopyrite.

To elucidate the nature of ore grindability, experiments were carried out to grind samples with a grain size of -3 + 0 mm in a laboratory ball mill of 40 ML type during the course of various times. Grinding was carried out with constant ball loading in the ratio of S:W:B = 1:0.75:8. The crushed ore samples were wet screened by the -0.074 mm class. The data obtained are presented in Fig. 1.

When enriching the copper-molybdenum ores, relatively coarse grinding is characteristic; the content of the grain-size class of 0.074+0 mm is in the range from 40% to 70% (Karnaukhov, 2007; Mergenbaatar, 2005). Thus, for copper-molybdenum ores of the Kalmakyr deposit in cyclone overflow, feeding the collective flotation cycle, 60% of the -0.074 mm class (Turakulov and *et al.*, 2019) is contained.

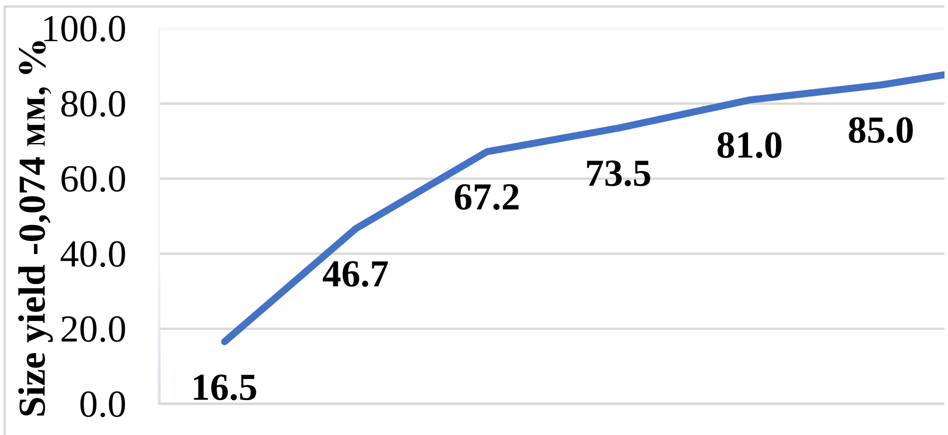

Figure. 1. Grindability curve of ore sample taken at the Kalmakyr deposit

To determine the optimal size of ore grinding during flotation, the experiments were carried out according to the scheme (Fig. 2), similar to that adopted for the flotation of copper-molybdenum ores using traditional collector reagents.

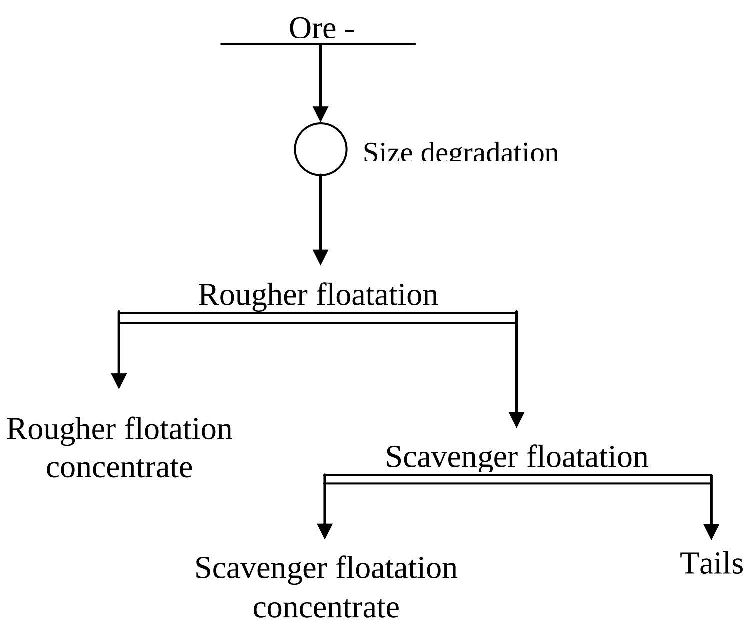

Figure 2: Technological scheme of bulk floatation

The size of ore grinding varied from 60 to 90% of the class -0.074 + 0 mm. At the same time, the reagent costs were (in g/t): for grinding - lime - 1200, spindle oil - 10, in the main flotation - potassium butyl xanthate - 20, T-92 - 20, in the control flotation - potassium butyl xanthate - 10, T-92 - 10. The ore sample of the Kalmakyr deposit is floated as efficiently as possible with an 80% grade of –0.074 mm. The results of the experiments are shown in table 1.
During the sample flotation of copper-molybdenum ores of the Kalmakyr deposit, experiments were carried out with the replacement of 50% of potassium butyl xanthate with new reagents and separately with a new shale oil reagent. The scheme included ore grinding to a particle size of 60% of the class -0.074 mm by analogy with the scheme of the AMMC copper processing plant, the rougher and scavenger flotation (Fig. 2). At the same time, the basic expenses of the reagents were (in g/t): for grinding - lime - 1200, spindle oil - 10, in the main flotation T-92 - 20, in the control flotation T-92 - 10.

Table 1: Ore flotation results with different grade contents of -0.074 mm

Product description	Output. %	Content. %				Extraction. %				Output cl. -0.074+0 mm. %
		Cu	Mo	Fe	S	Cu	Mo	Fe	S	
Concentrate of rougher flotation	9.9	3.63	0.0216	10.9	13.9	70.4	57.1	25.2	36.8	60
Concentrate of scavenger flotation	7.6	1.22	0.0071	12.6	21.3	18.0	14.3	22.1	43.2	
Tails	82.5	0.07	0.0013	2.7	0.9	11.6	28.6	52.7	20.0	
Ore	100.0	0.51	0.0037	4.3	3.7	100	100	100	100	
Concentrate of rougher flotation	11.2	3.64	0.0243	12.9	22.2	77.9	59.1	33.3	65.5	70
Concentrate of scavenger flotation	5.7	0.99	0.0068	7.8	7.8	10.8	8.4	10.2	11.7	
Ore	83.1	0.07	0.0018	3.0	1.0	11.3	32.4	56.5	22.8	
Initial sample	100.0	0.52	0.0046	4.3	3.8	100	100	100	100	
Concentrate rougher flotation	12.5	3.72	0.0238	12.8	20.8	86.2	63.9	35.3	67.2	80
Concentrate of scavenger floatation	4.4	0.67	0.0059	7.5	7.2	5.5	5.6	7.3	8.2	
Tails	83.1	0.05	0.0017	3.1	1.1	8.3	30.4	57.4	24.6	
Ore	100.0	0.54	0.0046	4.5	3.9	100	100	100	100	

The results of ore flotation experiments with a combination of traditional collecting agents with new reagents are graphically presented in Fig. 3 through extraction into the concentrate of the main flotation.
As a result of studies, it was found that the use of all tested collecting reagents, obtained on the basis of local raw materials, in the sample flotation of copper-molybdenum ores from the Kalmakyr deposit allows to get a rough concentrate (main flotation concentrate) with a Cu content of 5.23-11.32% and Mo - 0.0278-0.0521%. Copper extraction in the main flotation concentrates ranges from 88.2 to 93.3%, and molybdenum - from 53.2 to 83.7%. The results for copper are not only comparable to the results of the basic regime, but also for the degree of copper extraction in the concentrate of the main flotation, being higher by 17.7-22.9%. Comparable results are noted for the extraction of molybdenum, and in the case of using shale oil and PB-1, the extraction of molybdenum is higher by 14.0-26.6%.

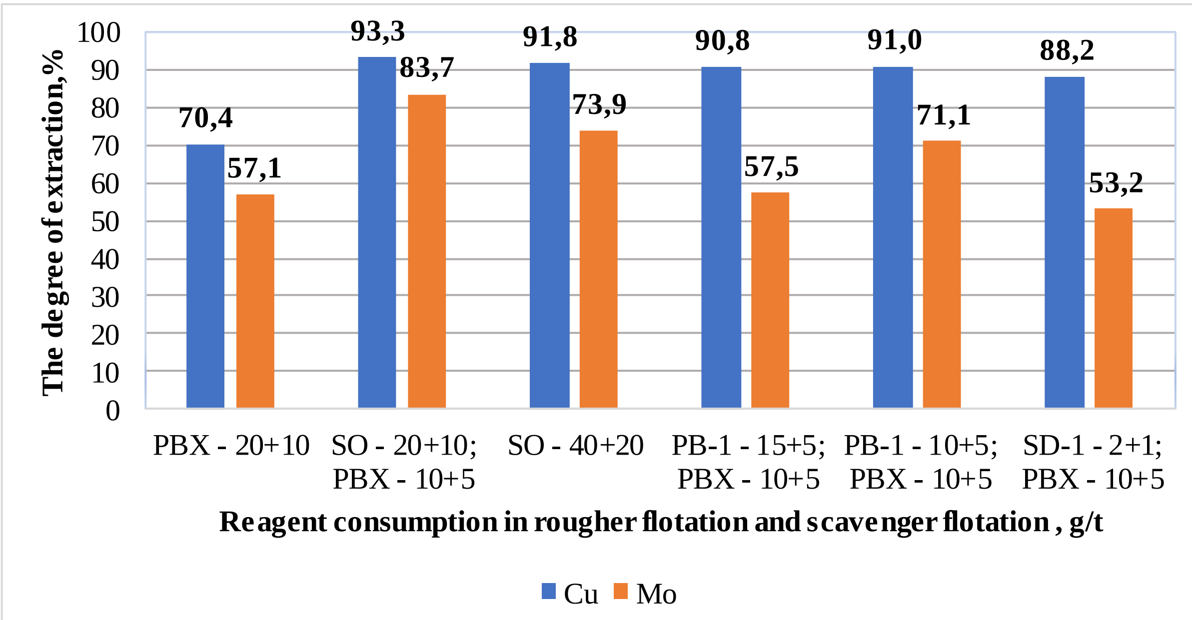

Figure 3: Extraction of Cu and Mo in comparative flotation experiments of a sample of copper-molybdenum ores with potassium butyl xanthate and new reagents shale oil, PB-1 and SD-1

Thus, the introduction of shale oil reagent in combination with potassium butyl xanthate, as well as separately in the enrichment of copper-molybdenum ores of the Kalmakyr deposit, provided an increase in copper extraction by 21.3-22.9%, molybdenum by 16.9-26.6%, and an increase in their content in the concentrate of the main flotation in 1.4-3.1 and 1.3-2.4 times, respectively.

CONCLUSION

As a result of the work for the study of copper-molybdenum ores of the Kalmakyr deposit, the following data were obtained:
1. The material composition of the sample of copper-molybdenum ores was studied.
2. The chemical composition and physical and chemical properties of the shale oil of the Sangruntau oil shale deposit as a local reagent were studied.
3. Data on the dependence of the increase in the control class of fineness on the grinding time were obtained.

4. Schemes of flotation of copper-molybdenum ores with reagents-collectors of various types were worked out. The classical scheme was based on the use of a sulfhydryl collector (butyl potassium xanthogenate) and an apolar collector (spindle oil). The main part of the research was related to the study of the possibility of partial or complete replacement of butyl potassium xanthogenate with reagents obtained from local raw materials – shale oil, PB-1 and SD-1.
5. For the first time, research has been conducted on the use of shale oil as a collecting agent for flotation of copper-molybdenum ores, as a result of which it has been established that shale oil is a highly effective collector when used both together with butyl potassium xanthogenate and separately.
6. Shale resin, as a liquid fraction of pyrolysis, includes a large number of individual compounds of various nature. Laboratory studies have shown that this product of oil shale pyrolysis can be used as a collecting agent, which is economically more profitable than imported reagents.
7. Due to the expected active development of oil shale processing facilities in Uzbekistan, a reliable raw material base will be provided in the near future for obtaining industrial quantities of shale oil and its use in the processing of solid minerals. "AMMC" JSC has sufficient resources for its own production of thermal decomposition of oil shale with a capacity of 10-15 thousand tons of shale per year, which will allow obtaining a sufficient amount of oil for the needs of the plant.

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