COMPARATIVE ANALYSIS OF MODERN FLOTATION REAGENTS IN BENEFICIATION OF COPPER-MOLYBDENUM ORES

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Abstract: The search for effective reagents for the flotation of non-ferrous metals from mineral raw materials is an actual problem. The article discusses the results of research on improving the technology of processing copper–molybdenum ores using a combined collector emulsion. The object of research was copper–molybdenum ore containing 0.43% copper and 0.0089% molybdenum. Copper minerals are represented by chalcopyrite 1.2% and chalcocite 0.015%, while covellite is present in a much smaller amount. The main mineral of molybdenum is molybdenite.The cycle of collective copper–molybdenum flotation includes the main flotation, control flotation, and three re-cleanings of concentrate. In the basic mode, the collective Cu–Mo concentrate was produced with the copper content of 16.25% with an extraction of 77.79% and with the molybdenum content of 0.45% with an extraction of 79.38%.Reaflot, thionocarbamate, and butyl xanthate were used in a ratio of 1:3:15 to prepare a combined collector agent. In order to produce the combined collector emulsion, the best degree of dispersion, which amounted to 99.5% of particles with a size of −3.6 μm, was chosen.During the Cu–Mo ore flotation using an optimally dispersed microemulsion of the combined collector agent, a collective Cu–Mo concentrate was obtained with a copper content of 18.2% with an extraction of 83.58%, and with a molybdenum content of 0.49% with an extraction of 88.46%.The use of a combined collector agent increases the extraction of copper into the collective Cu–Mo concentrate by 5.79%, while the extraction of molybdenum increases by 9.08%.

Keywords: beneficiation; flotation; ore; extraction; copper; molybdenum; combined collector agent.

СРАВНИТЕЛЬНЫЙ АНАЛИЗ СОВРЕМЕННЫХ ФЛОТАЦИОННЫХ РЕАГЕНТОВ ПРИ ОБОГАЩЕНИИ МЕДНО-МОЛИБДЕНОВЫХ РУД

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Аннотация: Поиск эффективных реагентов для флотации цветных металлов из минерального сырья является актуальной проблемой. В статье рассматриваются результаты исследований по совершенствованию технологии переработки медно-молибденовых руд с использованием комбинированной коллекторной эмульсии. Объектом исследования стала медно-молибденовая руда, содержащая 0,43% меди и 0,0089% молибдена. Минералы меди представлены халькопиритом 1,2% и халькоцитом 0,015%, в гораздо меньшем количестве присутствует ковеллит. Основным минералом молибдена является молибденит. Цикл коллективной медно-молибденовой флотации включает основную флотацию, контрольную флотацию и три повторных очистки концентрата. В базовом режиме был получен коллективный концентрат Cu–Mo с содержанием меди 16,25% и экстракцией 77,79%, а также с содержанием молибдена 0,45% и экстракцией 79,38%. Для приготовления комбинированного коллектора использовались реафлот, тионокарбамат и бутилксантат в соотношении 1:3:15. При флотации руды Cu-Mo с использованием оптимально диспергированной микроэмульсии комбинированного коллекторного агента был получен коллективный концентрат Cu-Mo с содержанием меди 18,2% с экстракцией 83,58% и с содержанием молибдена 0,49% с экстракцией 88,46%.Применение комбинированного коллекторного агента увеличивает экстракцию меди в коллективный концентрат Cu-Mo на 5,79%, а экстракцию молибдена на 9,08%.

Ключевые слова: обогащение; флотация; руда; экстракция; медь; молибден; комбинированный коллектор.

An increase in the efficiency of processing finely disseminated sulfide ores can be achieved through the use of improved reagent flotation modes, reagent processing, and new design solutions [1,2,3,4,5]. The improvement of reagent regimes is achieved using new selective flotation reagents, their combination, ultrasonic treatment of reagents, and new designs of flotation equipment.

The search for effective reagents for the flotation of non-ferrous metals from mineral raw materials is an actual problem. Based on the regulation of the water-repellent ability and surface activity, a collector agent of copper and precious metals, sample 225-5, was obtained, which is more efficient than the industrially used dialkyldithiophosphate reagent [6,7]. Sample 225-5 is a reagent modeled on a mixture of dialkyldithiophosphate with an extended hydrocarbon radical length and hydrophobizing component.

In the scientific research [8,9], the efficiency of phosphorus-bearing collector “PS” for the flotation of sulfide copper ores is shown. The crushing of the ore was about 60% of the class −0.074 mm. The efficiency of the flotation was controlled by the recovery of copper in the concentrate. At a consumption of the reagent “PS” 25 g/t, lime 0.75 kg/t, and frothing reagent T-92 85 g/t, the extraction of copper into the concentrate increases by 0.87%.

Scientists synthesized complexes of monohydroxamide and monohydrazide of 2-ethyl-hexenylsuccinic acid with nickel and copper [10,11,12,13,14]. The obtained reagents were tested on copper–nickel ore from the Pechenga ore deposits with a content of 0.49% Ni and 0.21% Cu. The use of the synthesized complex instead of the used aerofloat agent made it possible to obtain a collective copper–nickel concentrate with a nickel content of 7.5% with a recovery of 43.98%, and 4.3% copper with a recovery of 58.81%. The obtained results from the use of a complex of monohydroxamide and 2-ethyl-hexenylsuccinic acid monohydrazide in the flotation of sulfide ores indicate the prospects for their application.

Under the conditions of using non-ionic collectors, the known methods for determining their residual concentration are ineffective. The developed spectral technique provides measurement of the concentration of a nonionic collector—allyl ester of amylxanthogenic acid in the aqueous phase of the pulp of copper–molybdenum flotation. The technique was applied to calculate the optimal grinding size of copper–molybdenum ore at the Erdenet factory. This made it possible to correct the value of the optimal content of the finished size class and, at the same time, to increase the extraction of copper and molybdenum into the concentrate by 0.8%–1.3% [15,16].

An increase in the extraction of useful components from sulfide ores can be achieved using a combination of various collectors [17,18,19,20]. The optimal ratio of butyl xanthate and isobutyl dithiophosphate in a mixture with thionocarbamate was determined to increase the flotation rate of non-ferrous metals [21,22]. Increasing the proportion of butyl xanthate in any combination increases the flotation rate of all monominerals.

Scientists are conducting research on the creation of new dialkyldithiophosphates. It is found that the higher aerofloats C_{10}–C_{16} have the ability to reduce the surface tension at the liquid–gas interface, similarly to strong surfactants, and that aerofloat agents, starting from nonyl (C_9), are characterized by a slow establishment of equilibrium at the liquid–gas interface, especially at low flotation concentrations [23,24,25,26]. The main problems of copper-containing ore processing are: the low copper content in ore, the high content of slurry particles (up to 40% of the class size smaller than 10 microns), finding copper minerals in the form of ultrafine aggregates, and the absence of highly effective selective reagents. Therefore, this raw material is the most difficult with respect to extraction of nonferrous metal sulfides. For the solution of a problem application of new selective flotation reagents, their combination, ultrasonic processing of reagents, and new designs of flotation equipment are possible [25,27].

The difficulties of copper–molybdenum ores beneficiation include the need for the very fine grinding of beneficiation products, insufficient efficiency in separating sulfide minerals from rock minerals, and the need to use complex technological modes for separating sulfide minerals. Therefore, the problem of finding new technological methods and schemes for the copper–molybdenum ores beneficiation is an urgent one [28,29].

The main indicators of the flotation process—extraction and selective concentrate—when using collectors depend on the specificity of their interaction at the interface's solid–liquid (s-l) and liquid–gas (l-g). In this regard, researchers are focused on studying the influence of these factors and the mechanism of action of the collectors. The hydrophobizing action of collectors, including dialkyldithiophosphate, depends on the strength of the chemical bond, the "functional group of the reagent–mineral surface", and on the length and structure (hydrocarbon chain of normal and isostructure) of the radical.

Thus, research on forming more selective reagents and collectors than xanthates and dithiophosphates was performed at the Gintsvetmet Institute. A number of S-substituted dialkyldithiocarbamates have been synthesized. S-cyanoethyl, N and N-diethyldithiocarbamate (DECE), produced by the interaction of sodium diethyldithiocarbamate and acrylonitrile, have been recognized as the most promising for the flotation of copper–molybdenum and polymetallic ores.

Dialkyldithiophosphates forming weaker complexes with heavy metal cations (Cu, Ni, Zn, Mo, Fe, etc.) in comparison with xanthogenates are characterized by a greater difference with them in the strength of complexes with heavy metal cations, which provides a greater selectivity of dialkyldithiophosphates action both in the separation of nonferrous metal sulfides and in the separation of iron sulfides from them [21,24,25]. The higher surface activity of dialkyldithiophosphates at the interface l-g as compared to xanthogenates promotes the formation of small air bubbles and increases the flotation capability of fine particles.

Determining the effect of a combined collector on the extraction of copper and molybdenum (Cu–Mo) during the flotation of copper–molybdenum ores is the purpose of this work.

Materials and Methods

This work used mineralogical, electron probe, atomic emission spectral, X-ray phase, chemical and sieve analyses, as well as iodometric titration and flotation. The study used an atomic emission spectrometer: Optima 2000 DV (PerkinElmer Inc., Wellesley, MA, USA); an X-ray diffractometer: D8 ADVANCE (Bruker, Billerica, MA, USA); an X-ray fluorescent spectrometer: Venus 200 PANalytical B.V. (Almelo, the Netherlands); and an electron raster microscope: JEOL JXA-8230 (Tokyo, Japan).

Technological equipment was also used. The original ore was crushed on a jaw crusher (DMD160/100) to a coarseness of less than 2.5 mm at Bishkek Experimental and Experimental Plant of Geological Exploration Equipment. Then the ore was crushed in a ball mill (40ML-000PS) to a particle size of 94% of the class of less than

74 μm. Dispersion analysis of the crushed ore was carried out on a photometric sedimentometer (FSKh-6K). Flotation was carried out on a laboratory flotation machine with 0.5, 0.75, 1.0 and 1.5 L chambers.

The collective copper–molybdenum flotation cycle included basic flotation, control flotation and three concentrate purifications. The crushed ore in the form of a pulp with a density of 30%–35% solid was stirred in a flotation machine with flotation agents for a certain agitation time. The rotor speed was 1150 revolutions per minute. Then, at an air supply of 3.1 L per minute, the flotation of the ore was carried out. An emulsion of the combined reagent was prepared on the ultrasonic device UZDN-A1200T. The distribution of reagent particles after dispersion was studied using a laser particle analyzer (Winner2000E). A vibrating micromill, the “pulverisette O” from FRITSCH, was used to prepare samples of ore and enrichment products for chemical analysis.

Results and Discussion

The work on improving the copper–molybdenum (Cu–Mo) ore flotation technology from the Kazakhstan deposit using a combined collector agent was performed. The mineralogical analysis showed that the ore contains the minerals molybdenite, pyrite, chalcopyrite, chalcocite, quartz, albite and a number of less significant minerals.

The main copper minerals are chalcopyrite – 1.2% and chalcocite – 0.015%, with covellite present in a much smaller amount. The main mineral of molybdenum is molybdenite – 0.012%. Sulfide minerals of pyrite are present in amounts up to 0.5%.

According to the X-ray phase analysis, the content of the rock-forming minerals is 96% and is represented by quartz, albite, clinochlore, feldspar, chlorite, potassium microplagioclase and sericite.

In order to improve the technological performance of the flotation, test experiments were carried out on the flotation enrichment of the Cu–Mo ore using a combined reagent emulsion. The combined flotation agent is a mixture of sodium butyl xanthate, thionocarbamate and reaflot in an optimally selected ratio of 1:3:15. It was fed into the flotation process in the form of an emulsion produced in an ultrasonic disperser.

When using a combination of collectors in flotation, the mechanism of their interaction with the surface of minerals is determined by the characteristics of the surface of the minerals and the activity of each component of the collector. During dispersion, in addition to microbubbles, a microemulsion is formed, which, upon collision with slimy mineral particles, spreads and hydrophobizes their surface, improving the flotation process. Microbubbles, in turn, are more easily attached to such hydrophobized surfaces of slimy particles.

The higher surface activity of the combined reagent at the liquid–gas interface compared to xanthogenates promotes the formation of small air bubbles and increases the floatability of fine particles.

Studies on determining the dependence of the dispersion degree of the microemulsion of the base reagent sodium butyl xanthate and the combined flotation reagent on the degree of extraction of the slimy particles of copper and molybdenum during the mineral raw materials flotation were performed. The reagent dispersion time was 1, 2 and 3 min. The distribution of reagent particles after dispersion was studied on a Winner2000E laser particle analyzer, which is a laser diffraction particle size analyzer operating on the scattering principle. It is used to accurately determine the particle size distribution from 0.1 μm to 300 μm, with high sensitivity of the annular arrangement of photodetectors, which significantly increases the accuracy and repeatability of the measurements, with adjustable ultrasonic mixing and ultrasonic dispersion of the built-in liquid dispersion system.

The research results showed that when dispersing sodium butyl xanthate for 1 min, the particles with a size of less than 7.5 μm amount to 88.149%. When dispersing sodium butyl xanthate for 2 min, the particles with a size of less than 8.9 μm amount to 87.41%. When dispersing sodium butyl xanthate for 3 min, particles with sizes less than 8.6 microns amount to 91.032%. The measurement results show that the dispersion of butyl xanthate does not lead to a significant change in the particle distribution.

Conclusions

A reagent flotation mode using a combined collector agent, which is a mixture of reaflot, thionocarbamate and butyl xanthate in a ratio of 1:3:15, was worked out on a sample of Cu–Mo ore. The optimum degree of dispersion of the combined agent was 99.6% of the particles smaller than 3.7 μm.

Studies comparing the results with the base collector sodium butyl xanthate were also conducted. In the basic mode, a collective Cu–Mo concentrate was produced with a copper content of 16.25% with an extraction of 77.79%, and with a molybdenum content of 0.45% with an extraction of 79.38%.

With the use of a combined collector agent, a collective Cu–Mo concentrate was produced with a copper content of 18.2% with an extraction of 83.58%, and with a molybdenum content of 0.49% with an extraction of 88.46%.

The extraction of copper into Cu–Mo concentrate increases by 5.79% and molybdenum by 9.08% with the use of butyl sodium xanthate compared with the basic regime.

The use of a dispersed microemulsion also makes it possible to increase the degree of extraction of slimy copper particles into a Cu–Mo concentrate. The content of copper-containing sludge particles in the flotation tailings is reduced by 10.09% when using a combined collector agent.

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