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РАЗРАБОТКА МЕТОДОВ ОПРЕДЕЛЕНИЯ ФЛОТИРУЕМОСТИ МИНЕРАЛОВ ДЛЯ ЭФФЕКТИВНОГО ПРОЕКТИРОВАНИЯ ТЕХНОЛОГИИ ФЛОТАЦИИ

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Аннотация: снижение эффективности технологий переработки из-за сокращения доли руд с высоким содержанием ценных компонентов в минерально-сырьевой базе является актуальной проблемой для горно-обогатительной промышленности. Одним из направлений решения этой проблемы является использование современных методов исследования свойств материалов и особенностей производственных процессов для обоснования и выбора направлений в новых подходах к разработке технологий обогащения полезных ископаемых. В статье предлагается метод оценки гидрофобности минералов по результатам анализа их поверхностных свойств. В результате работы обоснован выбор смеси собирателей для флотации медно-никелевых руд на основании оценки поверхностных свойств.

Ключевые слова: медно-никелевые руды, флотация, сульфгидрильные собиратели, свободная энергия поверхности, краевой угол смачивания.

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Development of methods for determining the floatability of minerals for effective design of flotation technology

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Abstract: Reducing the efficiency of processing technologies due to the reduction in the share of ores with high content of valuable components in the mineral resource base is a pressing problem for the mineral processing industry. One of the directions for solving this problem is the use of modern research methods for studying the material properties and features of production processes to substantiate and select directions in new approaches to the development of technologies for mineral processing . The article proposes a method for assessing the mineral hydrophobicity based on the results of the analysis of surface properties. As a result of the work, the choice of a collector mixture for the flotation of copper-nickel ores was substantiated by the assessment of the surface properties.

Key words: copper-nickel ores, flotation, sulfhydryl collectors, free surface energy, contact angle.

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1. Introduction

Nowadays, one of the most pressing problems of the processing industry is the decline in the efficiency of technologies for the mineral raw materials separation. However, the high economic risks associated with field testing of new technologies significantly reduce the attractiveness of their implementatoin on an industrial scale [1, 2]. The solution to this problem lies in the application of new research methods, related to the study of the materials'properties and the characteristics of production processes with the purpose to substantiate profitability and efficiency at the project stage [3, 4].

A wide range of scientific works is focused on this problem. The first line of research focuses on the development and implementation of energy-saving ore dressing technologies based on the analysis of the strength properties of contrast materials [5—7]. The second line is the study of the introducing «deep» technologies in the mineral processing industry possibility [8—10]. In this case, the main goal is to intensify the main stages of the beneficiation process and to combine mineral processing operations with the methods of hydro- and pyrometallurgy [11, 12]. A good example is studies of microwave treatment of refractory gold-bearing material in the preliminary stages of flotation enrichment. Its purpose is to increase the degree of separation of sulfide minerals and change the sorption activity of ore minerals by processing with electromagnetic pulses [13—16]. Another cycle of works is devoted to increasing the automation degree of the mineral processing process through the use of digital technologies [17—18]. This approach improves the accuracy and speed of the control and sampling equipment, as well as it creates the ability to predict technological parameters on the basis of collected data [19—20].

Technologies that increase the efficiency of flotation make a special contribution to the development of mineral processing industry. However, a large number of influencing factors and running microscale processes in flotation significantly complicate the study of the process [21]. In the modern state of flotation, two main approaches to the description of the process have been formed: macroscale approach and microscale [22]. The essence of the macro-approach is as follows: application of «black box» models, where the main goal is to study the dependence between the operating conditions and flotation response. The advantage of this approach is the high reliability of the determined patterns, but the disadvantage is a narrow field of application of the created models [23—24]. As an example, the results of flotation kinetics and the approach to separation of flotation material into classes with different constants of flotation rate can be used to predict the degree of recovery in correlation with the time of flotation. This approach has proven itself in modeling flotation technological schemes and evaluating the effectiveness of the chosen scheme topology and equipment configuration [26—26]. In contrast to macro-models, micro-models describe a separate phenomenon or sub-process and its influence on the change of minerals' properties at flotation. Examples of such findings are studies of changes contact angles, free energy of minerals surface depending on the amount of sorbed reagent, as well as the structure of the frothy layer [27—28].

Copper-nickel sulfide ores are a promising object in the field of implementing new flotation technologies [29—30]. There are two main technological approaches for their beneficiation: bulk flotation scheme with subsequent selective flotation and direct selective flotation [31—32]. The main collectors used in the flotation of these ores are xanthates and alkyldithiophosphates. The main problem in processing such ores is in recovery of copper and nickel minerals into the bulk concentrate with their subsequent separation. The conditions of intergrowth of the copper and nickel minerals require additional grinding after the main flotation stage. Additional grinding leads to overgrinding and slurring of already disclosed copper minerals. Thus, the developed reagent suite at the stage of the main collective flotation should meet the condition of the maximum possible copper recovery in the concentrate [33—34].

The aim of the work was to evaluate the hydrophobization ability of the collector mixture in copper-nickel ore flotation based on the analysis of the surface properties of minerals.

2. Theoretical basis

In general, the probability of particle's reaching the concentrate launder is the complex probability of the following events [35]:

– Collision of a particle with an air bubble

– Fixation of the particle on the bubble

– Absence of detachment of the particle from the bubble.

One of the key factors influencing the probability of collision of a mineral particle with a bubble is the thickness of the layer of water molecules trapped by the electrostatic field of the double electric layer of the mineral surface . The thickness of the water layer is directly related to the surface free energy (hereinafter, SFE) [36].

The change in the SFE can be explained by the interfacial interactions that occur in flotation. These interactions can be divided into two different categories. The first category includes orientation, induction, and dispersion interactions of the molecules due to differences in the dipole moments of the interacting substances of the phases. The second category combines interactions caused by the formation of hydrogen bonds and charge transfer between surface species [37]. The former interactions are called dispersion interactions, the latter are called polar interactions.

The changes in the SFE can be established numerically by determining the surface tension at the liquid-solid-gas interface. In this work, the Owens-Wendt-Rabel-Kaelble method was used to determine the ratio of the surface free energy components. Numerical values of the surface tension components are determined from the solution of the system of equations [38]:

$$\begin{cases} \frac{\sigma_{L1}\left(\cos\theta_1+1\right)}{\sqrt[2]{\sigma_{L1}^{D}}}=\frac{\sqrt{\sigma_S^P}\sqrt{\sigma_{L1}^P}}{\sqrt{\sigma_{L1}^D}}+ \\ +\sqrt{\sigma_S^D}\,\frac{\sigma_{L2}\left(\cos\theta_2+1\right)}{\sqrt[2]{\sigma_{L2}^{D}}}= \\ =\frac{\sqrt{\sigma_S^P}\sqrt{\sigma_{L2}^P}}{\sqrt{\sigma_{L2}^D}}+\sqrt{\sigma_S^D}, \end{cases} \quad (1)$$

where: , are air-liquid surface tension values of analyzed liquids; ,are air-liquid polar surface tension values of analyzed liquids; ,are air-liquid disperse surface tension values of analyzed liquids;, are disperse and polar components of surface

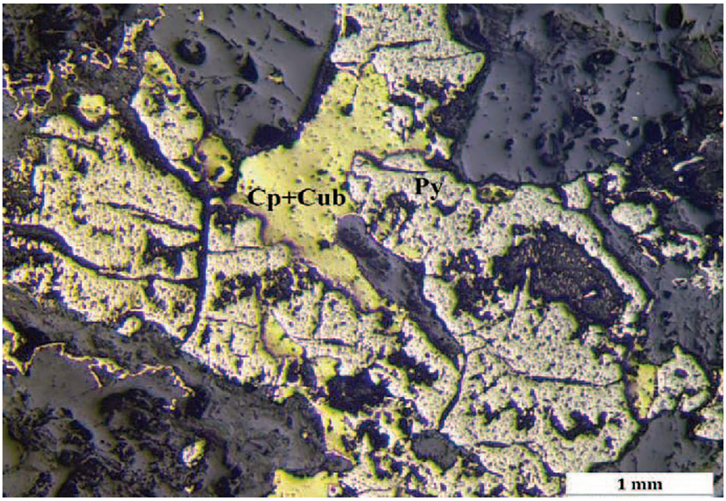

Fig. 1. Intergrowth structure of chalcopyrite and cubanite in the studied sample of the copper-nickel ore

free energy respectively;, are contact angles for analyzed liquids.

3. Materials and methods

The object of the study was a sample of copper-nickel ore (Fig. 1). The ore samples were already pre-grinded and had an 80% yield of –74 microns sieve class. The main copper ore minerals in the sample were chalcopyrite and cubanite. The main ore minerals of nickel in the sample were pentlandite, nickel-containing pyrrhotine. The content of copper was 0.91% and nickel was 0.64%.

The assessment of the hydrophobization ability of the collecting mixtures was carried out on the basis of the analysis of the surface properties The obtained results were confirmed by the results if a series of flotation experiments .

For the purposes of this work, samples of the chalcopyrite monomineral fraction were used as the main copper-containing mineral in the sample. Mixtures of potassium butyl xanthate (PNBX) with various alkyldithiophosphate-based compounds were chosen as the collectors: ammonium dibutyl dithiophosphate (ABDTP), sodium diisoctyldithiophosphate (SiODTP), sodium diisobutyl dithiophosphate (SiBDTP), sodium dibutyl dithiophosphate (SBDTP) in the ratio 1:1.

The essence of the analysis of surface properties consisted of the measurement of contact angles of water and diiodomethane on the surface of a sample of the monomineral fraction and the subsequent calculation of the SEP values using equation (1). The measurements were taken before and after the surface treatment by the collector mixtures described above.

A series of verification flotation experiments were performed for the collector mixtures described above . A 1% dextrin solution was used as a depressant at a rate of 80 g/t. The reagent «VS-1M», which is a mixture of alcohols and aromatic compounds, was used as a frother. The frother dosage during flotation was 30 g/t. The pH value during flotation varied between 9.4 and 9.6. Sodium carbonate was used as a pH regulator.

The surface properties of the minerals were investigated using Kruss DSA25 equipment. Analysis and measurements of contact angles were carried out in the software of the Kruss company.

Table 1
Experimental values of free surface energy and its components when treating the monomineral fraction with collecting mixtures of different compositions

№	Type of the collector's mix	Full SFE, mJ/m^2	Dispersion component SFE, mJ/m^2	Polar component SFE, mJ/m^2
1	Without treatment	61.39	22.96	38.43
2	PNBX + SBDTP	47.02	41.52	5.50
3	PNBX + ABDTP	35.86	32.35	3.51
4	PNBX + SIBDTP	48.65	29.25	19.40
5	PNBX + SIODTP	60.49	29.30	31.19

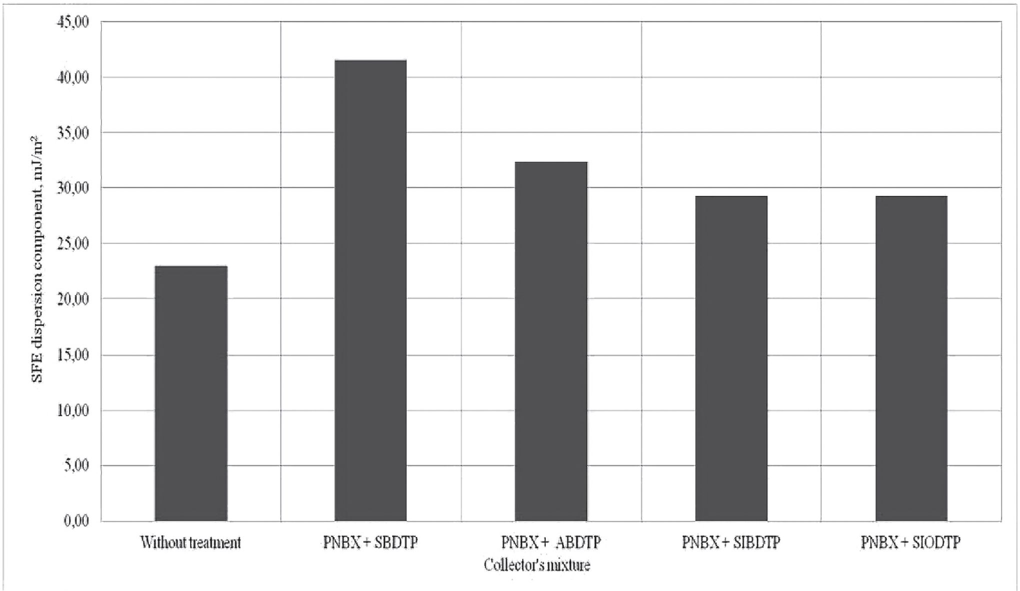

Fig. 2. Values of SFE dispersion component for the monomineral fraction surface treated by various collector mixtures

4. Results and discussion

The results of the study of the surface properties of the monomineral fraction treated by different collector mixtures are presented in Table 1. The graphical interpretation of the obtained results is presented in Fig. 2.

In the process of the analysis of the results obtained, it was found that the greatest change in the SFE was observed when the mixture of PNBX + ABDTP was applied. In comparison with the untreated surface, the change was amounted to 14.37 mJ/m^2. At the same time, the highest value of the dispersed SFE component corresponds to the application of a mixture of PNBX and SBDTP with a value of 41.52 mJ/m^2.

The decrease in SFE values is probably caused by physical and chemical interactions occurring between the collector molecules and the molecules of the mineral surface layer. A significant decrease in the polar component of the SFE is apparently due to the chemical sorption of sulfhydryl collectors on the sulfide surface. The sorbed reagent reduces the possibility of the formation of

Table 2
Results of flotation experiment series

Collector's mix	Cu grade,%	Cu recovery,%	Ni grade,%	Ni recovery,%
PNBX + SBDTP	3.35	74.66	1.62	55.78
PNBX + ABDTP	2.93	70.67	1.53	57.13
PNBX + SIBDTP	2.99	62.82	1.62	52.53
PNBX + SIODTP	2.87	70.32	1.43	54.24

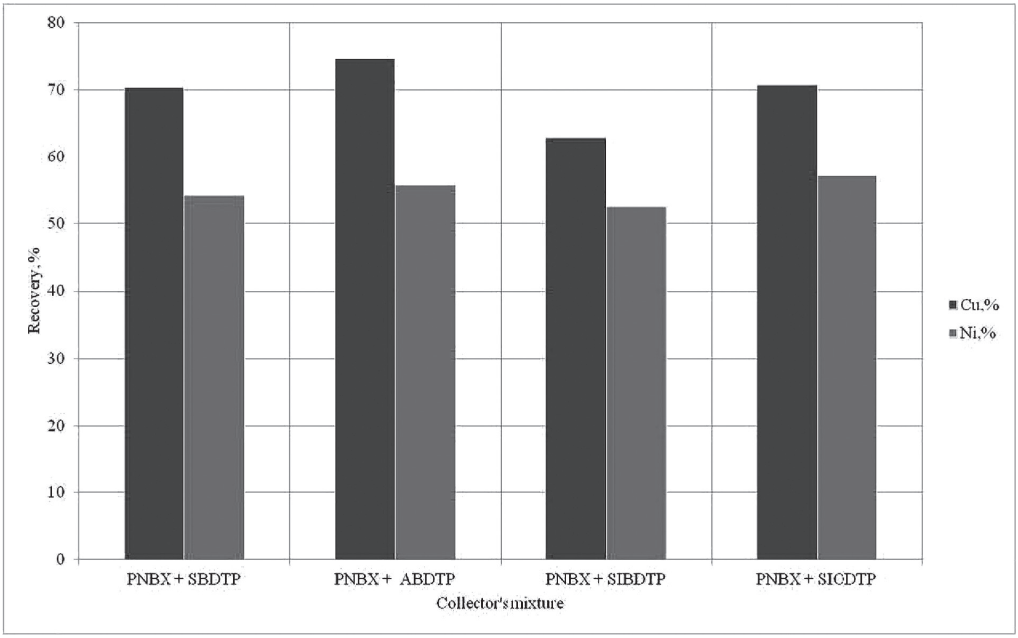

Fig. 3. Copper and nickel recovery values in concentrate for flotation tests series

the hydrate layer due to the electrostatic field of its apolar part. Thus, the value of the dispersion component of the SFE should increase on the surface treated with collectors. In this case, the probability of mineral particle collision with the air bubble and, consequently, the probability of flotation will correlate with the values of the dispersion components of the SFE.

The results of the flotation experiments series to verify assumptions are presented in Table 2. Graphical interpretation of the obtained results is presented in Fig. 3, 4.

During the test flotation experiments, the maximum value of copper recovery was obtained using SBDTP and PNBX mixture with a value of 74.66%.

Obtained results of the flotation experiments series confirm the assumption that there is a correlation between the established values of the surface free energy dispersion component and the flotation performance.

5. Conclusion

The need to increase the ores processing profitability requires increasing of the efficiency of the used beneficiation technologies. One of the promising directions for solving this problem

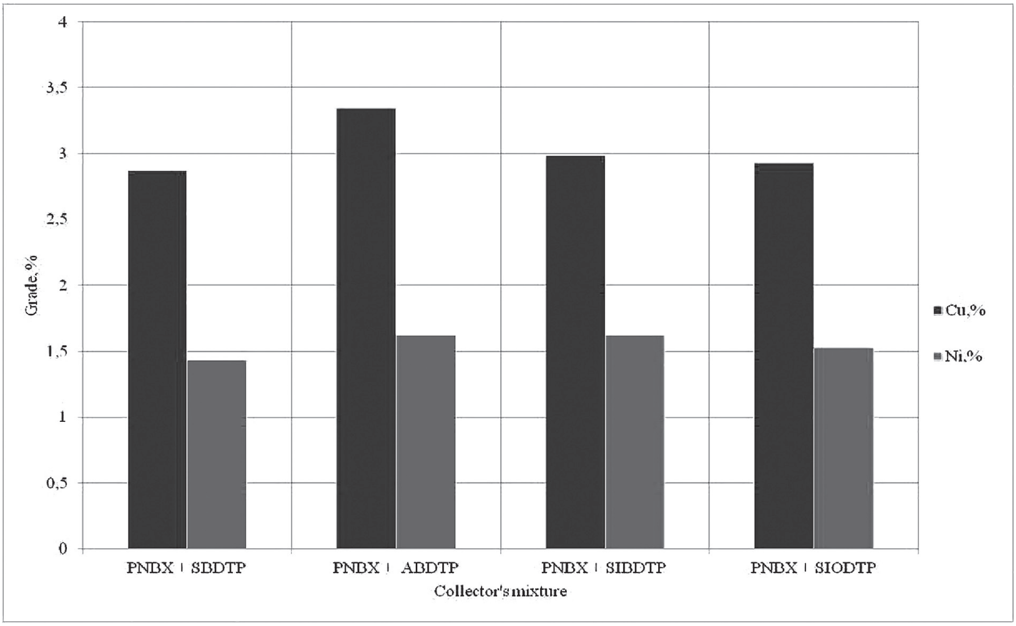

Fig. 4. Copper and nickel grade values in concentrate for flotation tests series

is the development of methods for a comprehensive assessment of the effectiveness of the proposed solutions based on the study of the physical and chemical properties of raw materials and features of technological processes.

In this work, we propose an approach to estimate the hydrophobization ability of several collection mixtures based on the analysis of the surface free energy of minerals. The samples of monofractions of copper minerals and samples of copper-nickel ore were the object of the study.

In the course of work, it was found that a necessary condition of high hydrophobiztion ability is a high value of the surface free energy of the dispersion component after treatment with a collector mixture. For chalcopyrite monofraction, the highest value of the dispersion component was observed when treated with a mixture of butyl potassium xanthathe and sodium dibutyl dithiophosphate. The obtained results were confirmed by a series of flotation experiment.

Thus, the proposed evaluation method can be used for selecting and justifying the reagent mode of flotation beneficiation of copper-nickel ores.

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