

Complexing Reagents Effect on Sulfide Ores Flotation

¹AKIMBEKOVA Bakhyt, Cand. Tech. Sci., Associate Professor, akimbekova.b@mail.ru8,

¹KAIYRBAYEVA Marzhan, Senior Lecturer, m_kaiyrbaeva@mail.ru,

¹*ZHORABEK Aigul, Master of Engineering, Senior Lecturer, aia86@mail.ru,

¹MALYBAEVA Mariash, Senior Lecturer, malybaeva2648@mail.ru,

¹Karaganda Technical University, Kazakhstan, 100027, Karaganda, N. Nazarbayev Avenue, 56,

*corresponding author.

Abstract. When copper-sulphide ores are dressed, lead is extracted into the copper concentrate, its increased content in the copper concentrate pollutes the atmosphere with the exhaust gases of the smelter. The paper discusses ways to reduce the toxic lead content in copper concentrate during flotation of copper sulfide ores. Selective flotation of galena occurs when hydrophobic elemental sulfur is formed on its surface, and hydrophilizing oxygen-containing compounds predominate on the surface of copper sulfides. One way is studying the relationship between the structure of organic and inorganic compounds, their adsorbability on the surface of minerals and the flotation properties of sulfide minerals. To study the structure of reagents effect on flotation of sulfide minerals, inorganic and organic compounds with several polar groups in the molecule are selected that are capable of forming complex compounds with metal cations. The presence in the molecule of several anionic groups enhances the depressing effect of the reagents, due to the mutual influence of atoms and groups. This contributes to selective flotation of minerals. The mineralogical analysis shows that sodium thiosulfate inhibits flotation of chalcocite and bornite. The presence of minerals and active ionic groups on the surface leads to activation of oxygen molecules in the boundary zone and to formation of a number of stable sulfur and oxygen compounds. In order to develop differences in the composition of the surface compounds of galena and copper sulfides (chalcocite, bornite, chalcopyrite), we studied the effects of two suppressant reagents: sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) and red blood salt $\text{K}_3[\text{Fe}(\text{CN})_6]$. Flotation of minerals is performed without a collector, based on the natural flotation of galena.

Keywords: complexing reagent, galena, chalcocite, selective flotation, extraction, thermogravimetric analysis, hydrophobization, hydrophilization, elemental sulfur.

Introduction

Studying the relationship between the surface properties of minerals, the structure of organic compounds, their adsorbability and flotation activity is becoming increasingly important.

Organic compounds containing several reactive groups in the molecule have a greater covalent bond, participate in the formation of a complex with cations of copper, lead and zinc metals, depending on the pH of the medium.

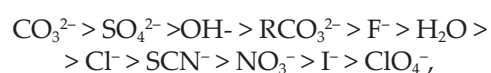
The presence of several anionic groups in the molecule (OH^- , COO^- и SO_3^{2-}) enhances the depressing effect of the reagents, since the mutual influence of atoms and groups is observed in the molecule. As a result of the shift of the electron density in the molecule, the mesomeric effect is enhanced, due to which a chemical bond is formed between the reagent and cations of the mineral surface, and intramolecular complex compounds are formed.

Hydroxyl ions displacing sulphhydryl collector ions hydrophilize the surface of the mineral. The hydrophilic surface of the mineral is characterized by the predominance of unsaturated ionic, atomic or polar bonds on it. On the contrary, the hydrophobic

surface of the mineral is characterized by the predominance of unsaturated molecular bonds on it, weakly interacting with the aqueous phase of the flotation pulp.

Hydrophobicity of minerals facilitating their flotation or hydrophilicity, which prevents the latter, is a measure of the activity of the mineral surface to interact with the aqueous and gas phases of the pulp. The result of this interaction is formation of a hydration shell on the surface of the mineral, the thickness of which corresponds to the size of many thousands of water molecules and reaches 0.1 microns. Hydration shells are formed in those cases when the binding energy between the water dipoles and the surface of the mineral is greater than that between the water dipoles.

The following row of descending shifts is qualitatively established:



that is, ions standing to the right of the water in this row do not form strong hydrogen bonds in the water, and those standing to the left form them [1].

Therefore, on the surface of sulfide minerals, the strongest hydrogen bonds will arise on the $\text{CO}_3^{2-} \rightarrow \text{O}_4^{2-} \rightarrow \text{OH}$ anions.

The ions causing degradation of water should form stronger hydrate layers, thereby enhancing hydrophilization of the mineral surface.

Taking into account this mechanism of action of reagents with the surface of minerals, the hydrophilizing properties of sulfosalicylic acid were studied. The carboxyl group and the sulfo group are chemically reactive groups. That is, the following mechanism of fixing compounds with such a structure is possible (Figure 1):

The group $-\text{COOH}$ can hold four water molecules, due to which a hydrogen bond is formed, the OH group binds three water molecules, so it is possible to form a hydrogen bond due to the presence of an OH group in the molecule, that is, molecules with such a structure are most likely to attach to the mineral surface, enhancing the wettability of the sulfide minerals surface.

Adsorption of heteropolar molecules and organic ions on the surface of hydrophobic molecules can occur in two ways: in the form of physical adsorption in the order of equalizing phases, which is associated with decreasing free energy at the interphase boundaries. With introduction of polar collectors or a foaming agent, the well-hydrated part with the functional group should be directed towards the liquid phase of the pulp, which will contribute to decreasing free energy, and the polar ends should be directed towards the mineral that has a covalent bond and is worse wetted by water. Such an orientation of the heteropolar compound could provide selective flotation of minerals [1].

In the interaction of flotation reagents with the aqueous medium of the flotation pulp, various processes occur, one of which is formation of soluble and sufficiently stable complex compounds on the surface of minerals.

The difference in the composition of the compounds formed on the mineral surface is provided by the unequal interactions of flotation reagents with active centers on the mineral surface. The most hydrated will be minerals with oxygen-

containing compounds on the surface of sulfide minerals. This problem can be solved by introducing selectively acting depressant reagents into the pulp.

The aim of the work is studying the effect of organic and inorganic compounds with several polar groups in a molecule on the selective flotation of copper sulfide ores.

Experimental part

Studying the effect of depressants of sulfosalicylic acid, sodium alizarin sulfonate and sodium thiosulfate on chalcocite, galena was carried out in a foamless flotation apparatus. The weight of the sample was 200 mg, the fineness of grinding was -0.074 mm. Soda was used as a regulator of the pulp alkalinity.

The surface of each mineral was treated with a 1% solution of the corresponding suppressant reagent within 1 minute and flotation was performed in a Halimond tube. Selective flotation of sulfide minerals without a collector is based on natural flotation of galena and regulation of the composition of surface compounds [2].

The spectrophotometric method of analyzing was used to measure the amount of elemental sulfur on the surface of galena and chalcocite after treatment with sodium thiosulfate. The absorption spectra of the hexane extract were measured on a spectrophotometer at the wavelength of 300-330 nm.

The degree of hydration of the galena and chalcocite surface was determined by the differential thermal analysis in combination with thermogravimetric analysis. The essence of this method is to measure the temperature of the endoeffect t_{onset} , the desorption heat Q_A and to determine the fraction of adsorbed moisture of the total n .

Results and discussion

The results of studying the effect of pulp pH and the consumption of sulfosalicylic acid reagents, sodium alizarin sulfonate and sodium thiosulfate on chalcocite, galena carried out in a foamless flotation apparatus are shown in Figures 3 and 4.

The optimal consumption of soda and flotation reagents under study was established by the maximum difference in the recovery of chalcocite

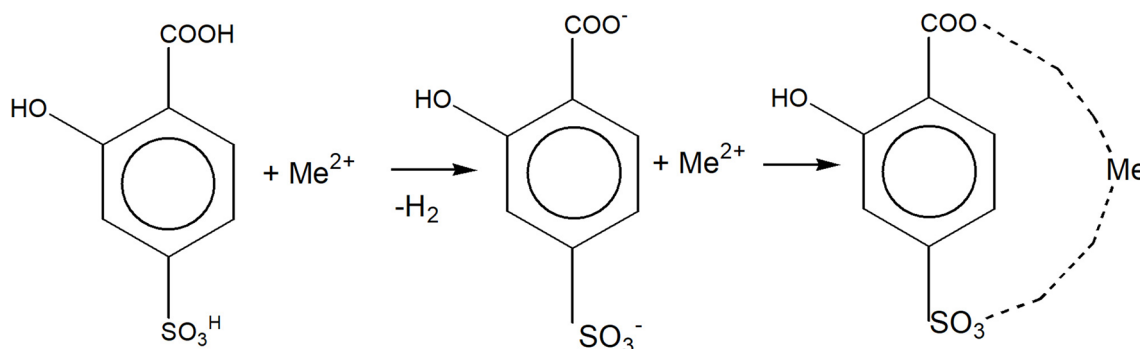


Figure 1 – Mechanism of sulfosalicylic acid interaction with the mineral surface cation

and galena at the 9.5 pH and the reagent consumption of 240 g/t (Figures 2 and 3). The largest selection of galena and chalcocine is observed with flotation of minerals with sodium thiosulfate.

The mechanism of the sodium thiosulfate action on the surface of chalcocine is to increase the oxygen-containing hydrophilic sites as a result of

thiosulfate complexes of copper formation. When interacting with the surface of galena, sodium thiosulfate slows down oxidation of elemental sulfur and, due to intramolecular oxidation-reduction, partially forms elemental sulfur. Elemental sulfur formed on the surface of sulfide minerals enhances hydrophobization [3, 4].

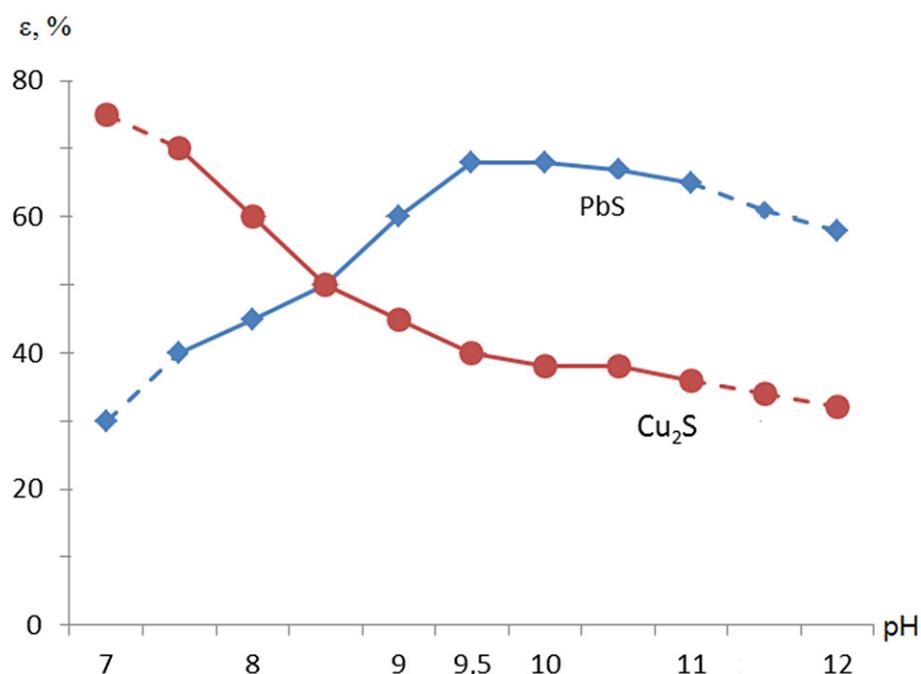
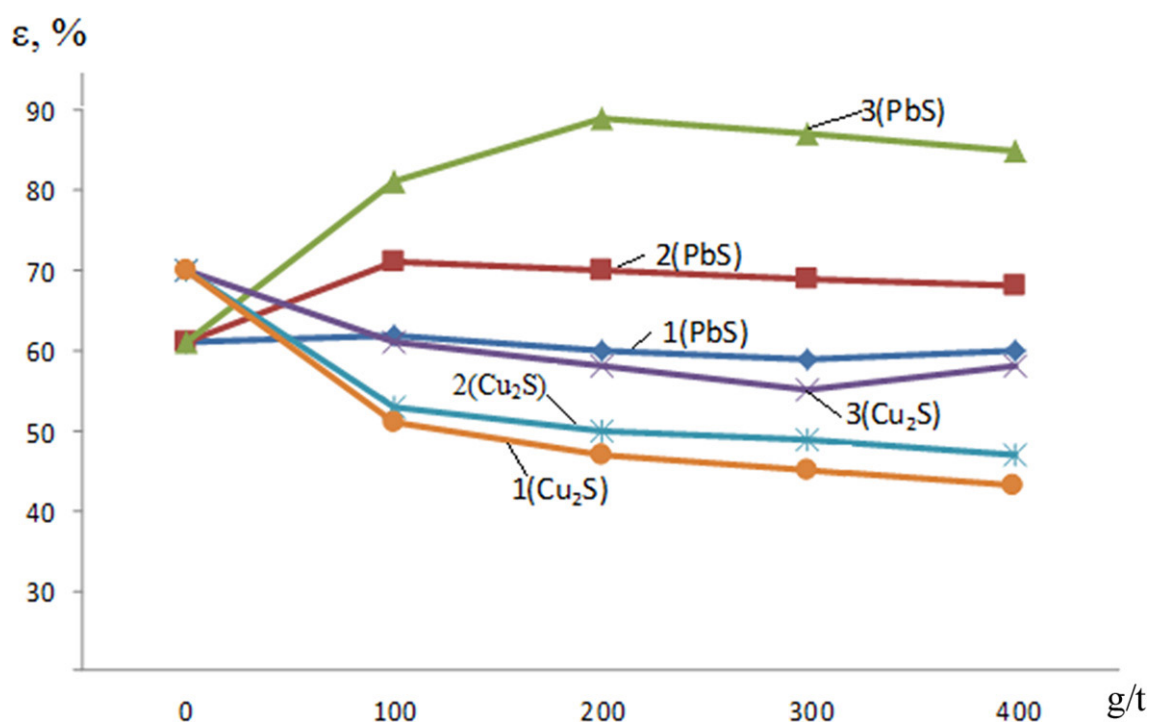


Figure 2 – The pulp pH effect on chalcocine and galena extraction



1 – sulfosalicylic acid; 2 – sodium alizarin sulfonate; 3 – sodium thiosulfate

Figure 3 – Flotation reagents consumption effect on chalcocine and galena extraction

The results of spectrophotometric analysis shows that when the surface of galena and chalcosine is treated with sodium thiosulfate, the amount of adsorbed sulfur on galena rises 2.5 times, and on chalcosine decreases 2 times; this contributes to hydrophilization of the surface of chalcosine. These results correlate with inhibition of chalcosine floatability.

As a result of mineralogical analysis of the concentrates, it turns out that thiosulfate suppresses secondary copper (chalcosine, bornite) minerals, and bornite is suppressed several times more (Figure 4, a), red blood salt suppresses only chalcosine (Figure 4, b). Chalcopyrite is not depressed by these reagents.

The mechanism of the sodium thiosulfate action is explained by the formation of free sulfur on the surface of galena as a result of intramolecular oxidation-reduction.

Thus, the results obtained show increasing the selective flotation of galena by the foaming agent in the presence of sodium thiosulfate and potassium ferrocyanide and decreasing natural flotation of bornite and chalcosine.

The correlation between galena and flotation of copper sulfide is determined by the sulfur content on their surface, thermal desorption of the molecule

and water, as well as the initial temperature of the endoeffect [5].

As a result of IR spectroscopy, the presence of elemental sulfur on the surface of galena and copper minerals, the degree of hydration of the minerals was determined by the differential thermal analysis. According to the results of the mineralogical analysis, it follows that sodium thiosulfate inhibits flotation of chalcosine and bornite [6].

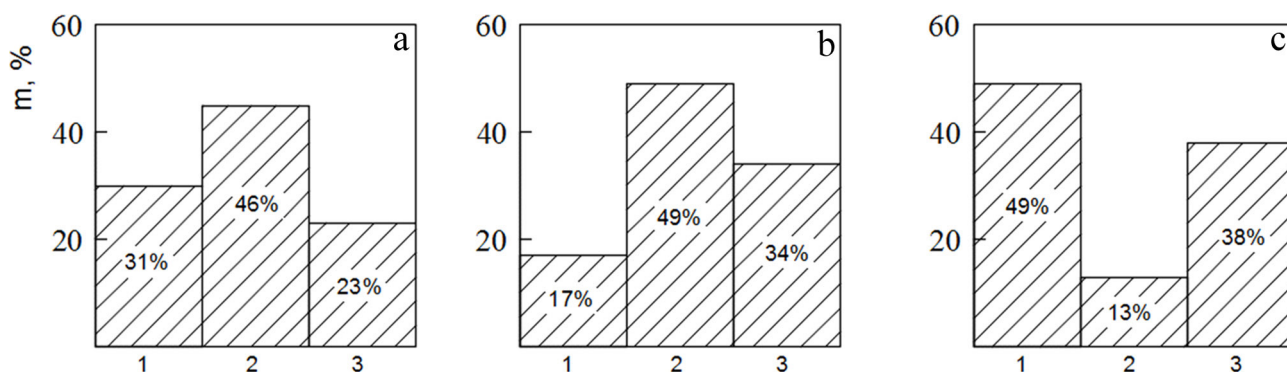
With decreasing the temperature of the endoeffect, hydrophobicity of the surface increases, since at a lower temperature there begins evaporating the adsorbed, in which the hydrogen bonds are weakened.

The results of the differential thermal analysis (DTA) are shown in Table.

The analysis of the tabular data shows that with the surface treatment of minerals with sodium thiosulfate there increases hydrophobicity of the galena surface in comparison with chalcosine. This indicates that moisture is physically adsorbed on the galena surface and the hydrogen bond energy is negligible.

Conclusions

Thus, from the obtained research results it can



1 – chalcosine; 2 – chalcopyrite; 3 – bornite (m is the mineral fraction)

Figure 4 – The ratio of changing copper minerals in the concentrate (a, b) in comparison with ore (c)

The results of the differential thermal analysis and thermogrammetry of galena and chalcosine

Mineral	Reagent	The endoeffect beginning temperature, t_n , °C	Fraction of the adsorbed water, n , %	Desorption heat, Q_n , st.unit
Chalcosine	Water	72	10.20	9.00
Galena	Water	47	7.00	3.98
Chalcosine	Sodium thiosulfate	60	12.00	11.25
Galena	Sodium thiosulfate	35	3.20	4.00
Chalcosine	Sodium alizarin sulfonate	65	6.00	8.16
Galena	Sodium alizarin sulfonate	28	1.80	3.68
Chalcosine	Sulfosalicylic acid	50	6.20	6.00
Galena	Sulfosalicylic acid	42	2.90	4.78

be concluded that the use of flotation reagents, sulfosalicylic acid, sodium alizarin sulfonate, sodium thiosulfate that contribute to changing the surface compounds of minerals, forms conditions for the selective flotation of galena and chalcocite. Among the studied reagents, sodium thiosulfate is the most effective one, it has a double effect: oxidative and reducing.

The use of sodium thiosulfate reagent $\text{Na}_2\text{S}_2\text{O}_3 \times 5\text{H}_2\text{O}$ in the dressing of copper sulfide ores improves the quality of copper concentrate, as a result of the possibility of galena separation into a separate product, by increasing hydrophobicity of its surface, and this leads to decreasing the lead content in the exhaust gases of the smelter.

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Сульфидті кендердің флотациясына кешен түзуші реагенттердің әсері

¹АКИМБЕКОВА Бакыт Базыловна, т.ғ.к., доцент, akimbekova.b@mail.ru8,

¹КАЙЫРБАЕВА Маржан Жаксыбаевна, аға оқытушы, m_kaiyrbaeva@mail.ru,

¹*ЖОРАБЕК Айгуль Аскарровна, т.ғ.м., аға оқытушы, aia86@mail.ru,

¹МАЛЫБАЕВА Марияш Кадыркеновна, аға оқытушы, malybaeva2648@mail.ru,

¹Қарағанды техникалық университеті, Қазақстан, 100027, Қарағанды, Н. Назарбаев даңғылы, 56,

*автор-корреспондент.

Аңдатпа. Мыс-сульфидті кендерді байыту кезінде мыс концентратынан қорғасын бөлініп алынады, оның мыс концентратындағы жоғары мөлшері атмосфераны мыс балқыту зауытының шығатын газдарымен ла-стайды. Мақалада мыс-сульфидті кендерді флотациялау кезінде мыс концентратындағы ұйымтас қорғасын құрамын төмендету тәсілдері қарастырылады. Галениттің селективті флотациясы оның бетінде гидро-фобты элементті күкірт пайда болған жағдайда өтеді, ал мыс сульфидтерінің бетінде гидрофилизациялай-тын оттегі бар қосылыстар басым болады. Органикалық және бейорганикалық қосылыстардың құрылымы, олардың минералдар бетінде адсорбциялануы және сульфидті минералдардың флотациялық қасиеттері арасындағы өзара байланысты зерттеу негізгі тәсілдердің бірі болып табылады. Сульфидті минералдардың флотациясына реагенттер құрылымының әсерін зерттеу үшін металл катиондарымен кешенді қосылыс-тар жасауға қабілетті молекуладағы бірнеше полярлық топтары бар бейорганикалық және органикалық қосылыстар іріктелді. Молекулада бірнеше анионды топтардың болуы атомдар мен топтардың өзара әсерінің салдарынан реагенттердің депрессиялық әсерін күшейтеді. Бұл минералдардың селективті флота-циясына ықпал етеді. Натрий тиосульфаты халькозин мен борнит флотациясын басады. Жер бетінде мине-ралдардың, белсенді иондық топтардың болуы шекаралық аймақта оттегі молекулаларының белсендірілуі-не және күкірт пен оттегінің бірқатар тұрақты қосылыстарының пайда болуына әкеледі. Галенит пен мыс сульфидтерінің (халькозин, борнит, халькопирит) беттік қосылыстарының құрамында айырмашылықты анықтау мақсатында екі реагенттердің: натрий тиосульфатының ($\text{Na}_2\text{S}_2\text{O}_3 \times 5\text{H}_2\text{O}$) және қызыл қан тұзының $\text{K}_3[\text{Fe}(\text{CN})_6]$ әрекеттері зерттелді. Минералдарды флотациялау жинағышсыз жүргізілді, ол галениттің та-биғи флотациялануына негізделген.

Кілт сөздер: кешен түзуші реагент, галенит, халькозин, селективті флотация, бөліп алу, термогравиметр-лік талдау, гидрофобизация, гидрофилизация, элементтік күкірт.

Влияние комплексообразующих реагентов на флотацию сульфидных руд

¹АКИМБЕКОВА Бакыт Базыловна, к.т.н., доцент, akimbekova.b@mail.ru8,

¹КАЙЫРБАЕВА Маржан Жаксыбаевна, старший преподаватель, m_kaiyrbaeva@mail.ru,

¹*ЖОРАБЕК Айгуль Аскарровна, м.т.н., старший преподаватель, aia86@mail.ru,

¹МАЛЫБАЕВА Марияш Кадыркеновна, старший преподаватель, malybaeva2648@mail.ru,

¹Карагандинский технический университет, Казахстан, 100027, Караганда, пр. Н. Назарбаева, 56

*автор-корреспондент.

Аннотация. При обогащении медно-сульфидных руд в медный концентрат извлекается свинец, повышенное содержание его в медном концентрате загрязняет атмосферу отходящими газами медеплавильного заво-

да. В статье рассматриваются способы снижения содержания токсичного свинца в медном концентрате при флотации медно-сульфидных руд. Селективная флотация галенита протекает при условии образования на его поверхности гидрофобной элементной серы, а на поверхности сульфидов меди преобладают гидрофилизующие кислородсодержащие соединения. Одним из способов является изучение взаимосвязи между структурой органических и неорганических соединений, их адсорбируемостью на поверхности минералов и флотационными свойствами сульфидных минералов. Для изучения влияния структуры реагентов на флотацию сульфидных минералов подобраны неорганические и органические соединения с несколькими полярными группами в молекуле, способные образовывать комплексные соединения с катионами металлов. Наличие в молекуле нескольких анионных групп усиливает депрессирующее действие реагентов, вследствие взаимного влияния атомов и групп. Это способствует селективной флотации минералов. Минералогическим анализом установлено, что тиосульфат натрия подавляет флотацию халькозина и борнита. Наличие на поверхности минералов, активных ионных групп приводит к активации молекул кислорода в пограничной зоне и к образованию ряда стабильных соединений серы и кислорода. С целью создания различий в составе поверхностных соединений галенита и сульфидов меди (халькозин, борнит, халькопирит) были исследованы действия двух реагентов подавителей: тиосульфата натрия ($\text{Na}_2\text{S}_2\text{O}_3 \times 5\text{H}_2\text{O}$) и красной кровяной соли $\text{K}_3[\text{Fe}(\text{CN})_6]$. Флотация минералов проводится без собирателя, основана на естественной флотирруемости галенита.

Ключевые слова: комплексообразующий реагент, галенит, халькозин, селективная флотация, извлечение, термобариметрический анализ, гидрофобизация, гидрофиллизация, элементная сера.

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