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IMPROVING THE TECHNOLOGY FOR PROCESSING OXIDIZED COPPER ORES FROM DEPOSITS IN KAZAKHSTAN

ҚАЗАҚСТАН КЕН ОРНЫНЫҢ ТОТЫҚҚАН МЫС КЕНДЕРІН ӨҢДЕУ ТЕХНОЛОГИЯСЫН ЖЕТІЛДІРУ

УСОВЕРШЕНСТВОВАНИЕ ТЕХНОЛОГИИ ПЕРЕРАБОТКИ ОКИСЛЕННЫХ МЕДНЫХ РУД МЕСТОРОЖДЕНИЙ КАЗАХСТАНА

Abstract. *The article presents research on improving the technology of processing oxidized copper ore, using the example of the Zharyktas deposit, in order to increase copper extraction due to sulfidization of oxidized copper minerals. The mineralogical, chemical and phase composition of the ore has been studied. When processing this ore using an improved technology, a concentrate with a copper content of 21.20% was obtained, which increased copper extraction by 42.77% compared to the basic technology.*

Keywords: *oxidized copper ores; flotation; reagents; concentrate; extraction.*

Аңдатпа. *Мақалада тотыққан мыс минералдарын сульфидтеу арқылы мыс алуды арттыру мақсатында Жарықтас кен орнының мысалында тотыққан мыс кенін өңдеу технологиясын жетілдіру бойынша зерттеулер келтірілген. Кеннің минералогиялық, химиялық және фазалық құрамы зерттелді. Бұл кенді жетілдірілген технология бойынша өңдеу кезінде құрамында мыс мөлшері 21,20% болатын концентрат алынды, бұл мыс өндіруді базалық технологиямен салыстырғанда 42,77 %-ға ұлғайды.*

Түйін сөздер: *тотыққан мыс кендері; флотация; реагенттер; концентрат; экстракция.*

Аннотация. *В статье приведены исследования по усовершенствованию технологии переработки окисленной медной руды, на примере месторождения Жарыктас, с целью повышения извлечения меди за счет сульфидизации окисленных медных минералов. Изучены минералогический, химический и фазовый состав руды. При переработке данной руды по усовершенствованной технологии был получен концентрат с содержанием меди 21,20 %, что увеличило извлечение меди на 42,77% по сравнению с базовой технологией.*

Ключевые слова: *окисленные медные руды; флотация; реагенты; концентрат; извлечение.*

Introduction. In the Republic of Kazakhstan, there is currently an acute problem of providing copper industry enterprises with high-quality mineral raw materials due to the depletion of the mineral resource base. According to the Ministry of Industry and New Technologies of the RK, reserved reserves of copper and polymetals in Kazakhstan remain for 10-15 years (Goncharov 2022).

In recent years, oxidized and mixed copper ores from such deposits as Aktogay, Kounrad, Benkala, Nurkazgan, Shatyrkul, Karchiga, Taskora, Borly, Ayak-Kodzhan, Bozshakol, Baitemir, Beschoku, Zhezkazgan, Vavilonskoe have been investigated to replenish the mineral resource base of copper in the Republic of Kazakhstan.

Features of the material composition of oxidized and mixed ores of non-ferrous metals predetermine their technological properties. One of the main features of the material composition is the complexity of their mineral composition. The mineralogy of oxidized and mixed ores is much more extensive than the mineralogy of sulfide ores, they have a finer structure and are very difficult for enrichment (Kenzhalyiev 2024 - Bakov 2000).

The solution to the problem of processing oxidized copper ores by the flotation method is seen in changing the properties of oxidized minerals in the direction of surface hydrophobization. Joint flotation of sulfide and oxidized copper minerals in the presence of a sulfidizing agent in the case of depression of iron sulfides with lime is carried out only at a low degree of oxidation and a variable content of oxidized copper in the ore, as, for example, at the Almalyk, Balkhash processing plants and at the “Marcopper” factory. Researchers are actively engaged in the development of new methods and enrichment schemes, the synthesis of highly efficient flotation reagents. One of the methods for solving the problem is the chemical modification of minerals through sulfidization, as a result of which oxidized minerals are converted into sulfide minerals with a hydrophobic surface. Various sulfidizing reagents can be used to make such a transformation. Among them is sodium sulfide. The effectiveness of the action of sodium sulfide is also determined by the release of elemental sulfur on the surface of the sulfided mineral as a result of the oxidation of the sulfidizing agent. At the same time, elemental sulfur plays the role of an additional surface water repellent. The effect of preliminary sulfidization with this reagent on the flotation of oxidized copper ore was studied. The experiments were carried out under optimal flotation conditions: the degree of ore sulfiding is 40%; consumption of xanthate is 400 g/t, blowing agent is 100 g/t of ore. Also, for comparison, experiments were carried out on flotation without sulfidization of the ore. It was found that the preliminary sulfiding of the ore with a reagent based on mechanically activated sulfur has a positive effect on the results of flotation - the quality of the concentrate increases by 0.74%, the extraction of copper into the concentrate increases by 30% (Abramov 2005- Omarova 2015).

In VNIITsvetmet, studies were carried out on the flotation enrichment of mixed copper ores on a sample of one of the sections of the Zhezkazgan deposit. According to the data of phase chemical analysis, copper in this sample is represented by 45.8% rel. oxidized forms and 54.2% rel. – sulfide forms (including in the form of secondary sulfides 45.8% rel., primary – 8.4% rel.). After a series of tests on the selection of flotation reagents, potassium amyl xanthate was used as a collector, and methylisobutylcarbinol was used as a blowing agent. Sodium sulfide was used as a sulfidizing agent in experiments to develop the conditions of the main flotation. According to the developed scheme of ore enrichment in laboratory conditions, a copper concentrate was obtained with a copper content of 31.32% with an extraction of 74.47% (Sherembaeva 2014-Gusev 2018).

Thus, the relevance of the research topic lies in the fact that the most difficult objects for processing are mixed and oxidized copper ores, which make it difficult to obtain high technological performance to produce high-quality homonymous concentrates or a high extraction of the main valuable components.

In this regard, in order to improve the technology of processing oxidized copper ore, the ore of the Zharyktas deposit was studied in order to increase copper extraction due to sulfidization of oxidized copper minerals (Gusev 2018-Chernousenko 2019).

Materials and methods of research. Samples of oxidized copper ore from the Zharyktas deposit were examined for mineral and petrographic studies. The slots and anschlyphs were studied using an Olympus BX-51 optical microscope, as well as an Olympus SZX16 stereo microscope. X-ray diffraction analysis was performed on a BRUKER D8 ADVANCE X-ray diffractometer. The DIFFRAC.EVA universal program was used to process X-ray diffraction data.

Results and discussion. According to mineralogical analysis, the sample of copper ore is represented by core material, rocks are dark gray, gray, brownish gray and brown in color with a massive texture. The rocks are fragmented and riddled with numerous veins. Oxidized copper minerals are visible in the lumpy material. They are mainly represented by malachite, chrysocolla is marked in the form of single nests. Ore minerals are developed along the cracks of the rock, forming thin filamentous veins. Rare inclusions in the breed were also noted. Malachite forms leaky, less often concentric and ray-shaped formations along the cracks. The most characteristic samples are shown in Figure 1.

Figure 1. General view of the rocks of the copper ore sample of the Zharyktas deposit
Note – compiled by the authors

The selected samples were used to make slots and full plates, which were studied using an Olympus BX-51 optical microscope, as well as an Olympus SZX-16 stereomicroscope. The average sample was also studied using X-ray diffraction analysis performed on a BRUKER D8 ADVANCE X-ray diffractometer. The DIFFRAC.EVA universal program was used to process X-ray diffraction data. The results of diffractometric (X-ray diffraction) analysis are shown in Figure 2.

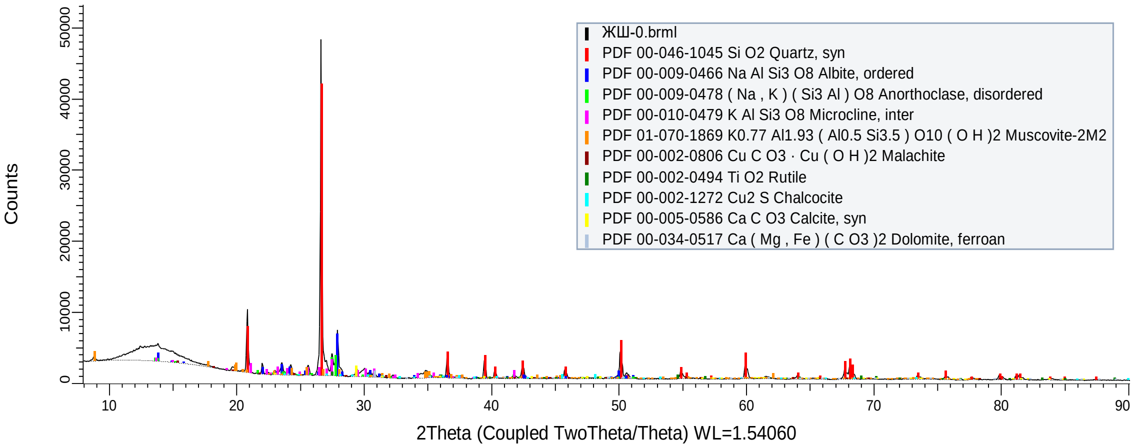

Figure 2. Results of diffractometric (X-ray diffraction) analysis of a sample of copper ore from the Zharyktas deposit

Note – compiled by the authors

Based on the results of X-ray diffraction analysis, as well as data from mineralogical and petrographic studies, it was found that quartz, feldspar, mica minerals predominate in the sample. Feldspars are represented by albite, microcline and orthoclase. Micaceous minerals are mainly represented by muscovite. Calcite and dolomite are noted among the carbonate rocks. Ore minerals in the sample of the studied ore from the Zharyktas deposit are represented by oxidized copper minerals (malachite, chrysocolla, tenorite), as well as secondary sulfide minerals (chalcocite, covellite, bornite). Rutile grains were also noted in the sample. Iron hydroxides and sulfide minerals (pyrite, chalcopyrite) were found in the form of single grains. The percentage of minerals in the sample is shown in Table 1.

Table 1. Mineral composition of copper ore samples from the Zharyktas deposit

The mineral	Content, %
Quartz	50,75
Feldspars	24,60
Micaceous minerals	18,20
Carbonate minerals	3,85
Oxidized copper minerals	0,3
(malachite, chrysocolla, tenorite)	0,2
Secondary copper minerals	0,1
Rutile	Single grains
Sulfide minerals	Single grains
Iron hydroxides	2,00
Note – compiled by the authors	

Rocks in petrographic terms are represented by lavas and lavobreccias, as well as tuffs of rhyolite-rhyodacite composition. In general, almost the same initial rock is visible in all rocks, represented by porphyry of acid composition (rhyolite or rhyodacite).

The oxidized copper minerals in the sample are dominated by malachite. It is developed both along the cracks of the rock, forming a veined mineralization, and in the rock itself with the formation of a rare, uneven interspersed mineralization (Figure 3).

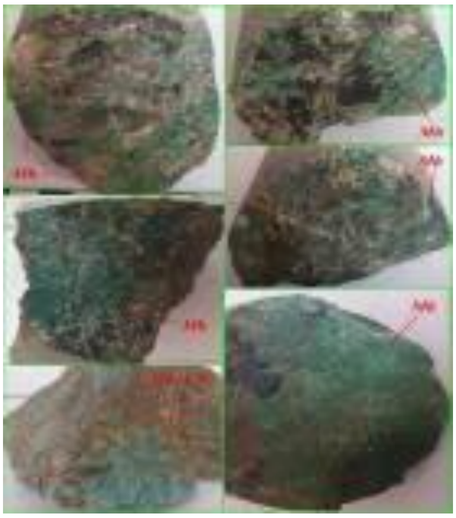

Figure 3. Inclusions and sintering forms of malachite made by cracks in rocks

Note – compiled by the authors

In the interspersed mineralization, malachite is developed in the form of xenomorphic clusters, rare tabular and ray-shaped grains, clusters of grains are also noted. The grain size ranges from 100-150 microns to 0.3-0.5 cm, less often larger clusters up to 1.5-2 cm are noted. Concentric clusters of malachite are marked as single grains. In addition to malachite, tenorite is also noted in association with chalcosine. Upon detailed examination, literally single nests of malachite in association with chrysocolla were noted in the sample. Chrysocolla has not been found in the form of independent grains.

In addition to oxidized copper minerals, secondary copper minerals are also shown in the sample. They are mainly represented by chalcosine, to a lesser extent covellin and chalcosine are manifested. The most intense interspersed mineralization tends to tuffs. Only single grains of covellin and chalcosine developed in the form of inclusions in tonsils, clusters of quartz, less often quartz-carbonate composition were noted in the catches (Figure 5). The size of such tonsils is 12-115 microns. The size of chalcosine and covellin grains in tonsils ranges from 1-3 microns to 12-17.5 microns. Single independent chalcosine grains with a size of 5-21 microns were also noted, sometimes developed in association with bornite and chalcopyrite (Figure 4).

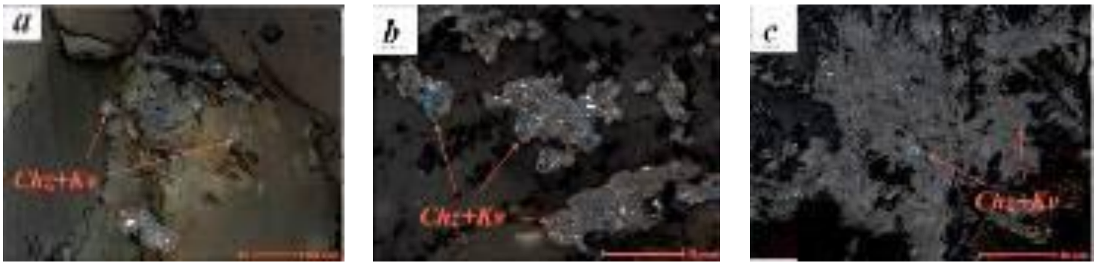

Figure 4. Polished section: a-g – amygdules composed of grains of chalcosine and covellin; d-e – single grains of chalcopyrite, pyrite and bornite

Note – compiled by the authors

In tuffs, however, a more intense interspersed mineralization is manifested. It is represented by isometric, xenomorphic, slightly angular chalcosine grains (Figure 5, a). Their size ranges from 25-50 microns to 360-580 microns. Chalcosine is developed in association with bornite, covellin and chalcopyrite. Covellin is presented in the form of needle-like, paniculate formations of chalcosine. Bornite is manifested mainly in the central part of chalcosine in the form of xenomorphic formations (Figure 5, b, c). Small grains of covellin are developed in association with bornite.

Needle-like, lamellar structures of chalcopyrite decay are also noted in bornite (Figure 5, c, d). In addition, chalcopyrite is manifested as independent large grains in association with chalcosine. In such associations, chalcosine forms a kind of chalcopyrite rim (Figure 5, e). Both a monomineral margin (chalcosine proper) and a close association of chalcosine with covellin, less often with tenorite, were noted (Figure 5, e).

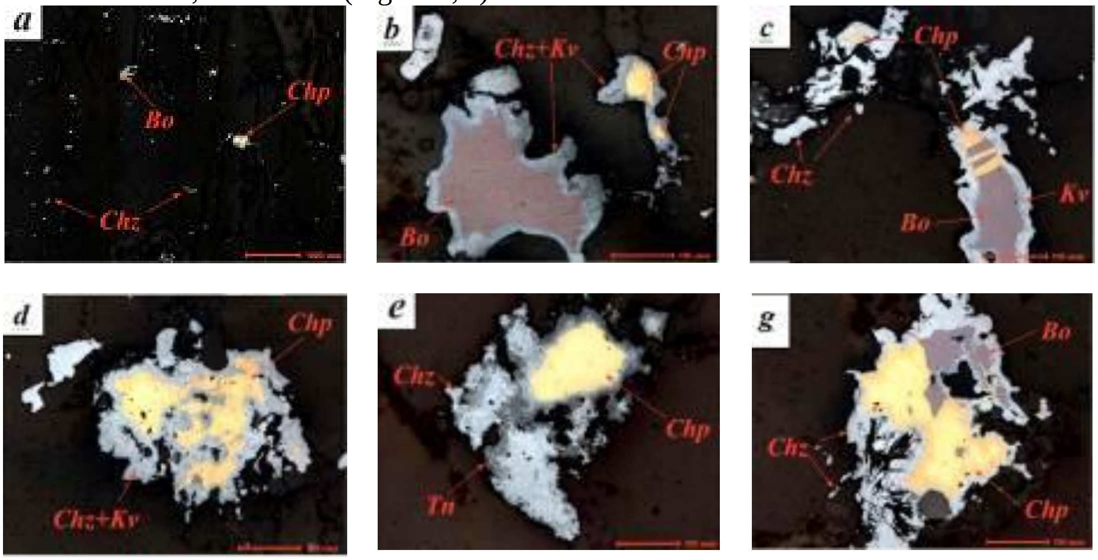

Figure 5. Polished section. Disseminated mineralization in tufas: a – dissemination of chalcocite grains in association with bornite and chalcopyrite; b – chalcocite grains, their central part is made of chalcopyrite and bornite; c, g – chalcocite grain in association with bornite, in bornite, decay structures composed of chalcopyrite; d – chalcopyrite grain with a chalcocite border, acicular covellite grains developed along chalcocite; e – chalcopyrite in association with chalcocite and tenorite

Note – compiled by the authors

The results of chemical and phase chemical analysis of the initial sample of copper ore from the Zharyktas deposit are shown in Tables 2 and 3.

Table 2. Chemical composition of a sample of copper ore from the Zharyktas deposit

Component	Content, %	Component	Content, %
Cu	0,50	K	3,32
Fe	1,16	Ba	<0,2
Au, г/т	0,040	Mn	0,016
Ag, г/ т	2,0	Ca	1,14
Zn	<0,01	Al	6,01
Pb	<0,01	Mg	0,29
Na	1,22	Te	<0,0020
SiO_2	70,66	Bi	0,0028
$S_{общ.}$	<0,1	Re	<0,00045
As	<0,030	S_{SO4}	<0,1
Cd	<0,002	Sb	<0,0050
Ge	0,0003	Cr	0,0010
Note – compiled by the authors			

Based on the results of studying the material composition of the studied sample of oxidized copper ore, it was established:

– the copper content in the ore is 0.50-0.53%, of which 64.4% rel. represented by oxygen-containing compounds, 30.0% rel. secondary sulfides and 5.6% rel. primary sulfides;

– the content of iron in the ore is 1.16%, calcium – 1.14%, magnesium – 0.29%, aluminum – 6.01%, sodium – 1.22%, potassium – 3.32%, silicon dioxide – 70, 66%, total sulfur – less than 0.1%, gold – 0.04 g/t, silver – 2.0 g/t;

– petrographically, the ore sample is composed of lavas, lava breccias and tufas of rhyolite (rhyolite dacitic) composition;

– the following minerals predominate in the sample: quartz, feldspars and micaceous minerals;

– copper minerals in the sample are represented by oxidized (malachite, chrysocolla, tenorite), secondary sulfide minerals (chalcocite, covellite, bornite) and single grains of chalcopyrite;

– malachite predominates among the oxidized minerals. It is developed in the form of xenomorphic, ray-shaped and concentric accumulations, as well as in the form of veinlet mineralization. Vein mineralization is confined to rock cracks;

– secondary minerals are represented by chalcocite, bornite, and covellite. It should be noted that in lavas (lavobreccias) chalcocite and covellite are developed in the form of rare amygdala-shaped accumulations. The amygdules are composed of quartz, less often quartz-carbonate aggregate. Intense dissemination of chalcocite and covellite grains is developed in them. The tufas contain more intense dissemination composed of chalcocite proper. Bornite, covellite and chalcopyrite are developed in association with chalcocite;

– a detailed study noted a small grain of native gold.

Basic technology the enrichment of oxidized copper ore is carried out according to the scheme shown in Figure 6.

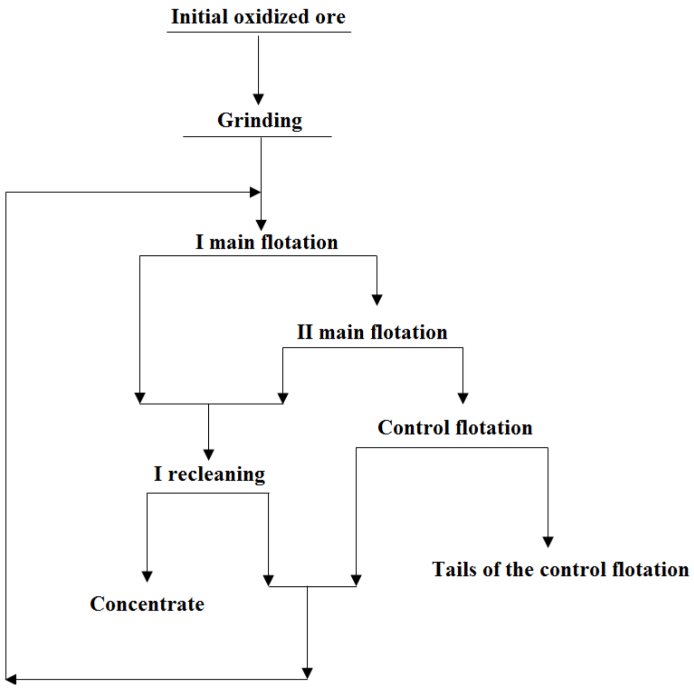

Figure 6. Basic scheme of enrichment of oxidized copper ore

Note – compiled by the authors

When processing ore according to this scheme, a concentrate with a copper content of 22.1% was obtained while extracting copper of 22.96%. The copper content in the tailings was 0.38%.

The proposed improved technology enrichments of oxidized copper ore of the investigated ore of the Zharyktas deposit with preliminary sulfidization was carried out according to the scheme including:

- ore grinding to a fineness of ~80% class minus 0.071 mm;
- basic sulphide flotation;
- main and control oxidized flotation;
- two recleanings of the crude concentrate of the main sulfide and main oxidized flotation;
- middling flotation of the concentrate of the control oxidized flotation and tailings of the first cleaning. The middling flotation concentrate was sent to the first cleaning.

Technological tests to determine the optimal size of ore crushing were carried out on a laboratory ball mill of the roller type with a size of 150x215 mm at W:T:W = 1:0.6:9 (T:W:W is the ratio of solid to liquid and to ball loading). The weight of the initial sample is 1 kg by dry weight, the pulp density is ~ 60% solid, the working volume of the mill is 3.0 liters. The results of the ore crushing tests are shown in Table 3 and Figure 7.

Table 3. Change in the granulometric composition of a sample of copper ore from the Zharyktas deposit during grinding in a laboratory ball mill

Size class, mm	Output of the class, % at the grinding time						
	0 min	10 min	20 min	30 min	40 min	50 min	60 min
minus 0,071	9,02	25,9	37,2	54,0	74,0	88,1	94,1
minus 0,045	7,17	18,8	27,1	39,1	53,0	65,9	75,2
Note – compiled by the authors							

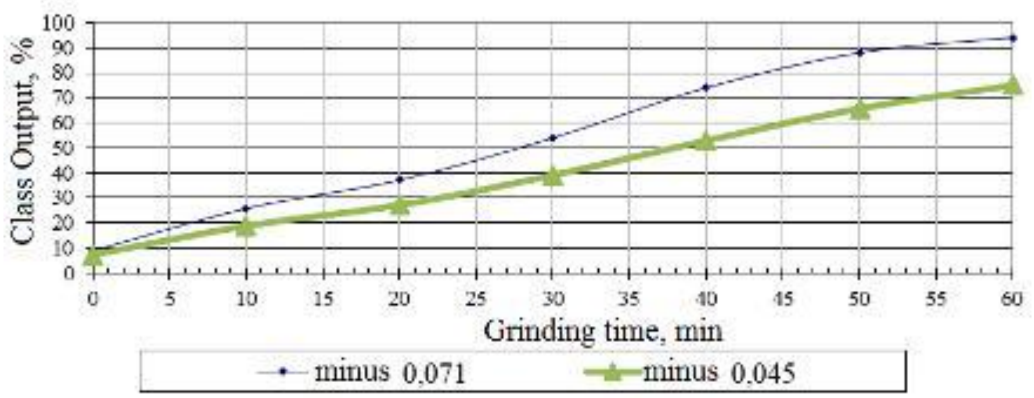

Figure 7. Dependence of the degree of grinding of a sample of copper ore from the Zharyktas deposit on the duration

Note – compiled by the authors

When grinding ore from 37.2 to 94.1% of the -0.071 mm class, the extraction of copper into the concentrate of the main flotation changes from 20.7 to 25.9%. At the same time, the copper content in the rough concentrate varies between 3.16-7.34%. The experimental results showed that the optimal size for ore flotation can be considered to be ~ 80% of the class minus 0.071 mm.

Research on flotation enrichment was carried out on laboratory flotation machines of the "Mechanobr" type with a chamber volume of 3.0 dm3.

The processing of oxidized copper ore from the Zharyktas deposit was carried out according to the scheme shown in Figure 8 and the results obtained are shown in Table 4. The reagent consumption was: sulfidizer (Na2S) – 620 g/t; collector – (SBX) – 120 g/t; foamer (MIBC) – 65 g/t.

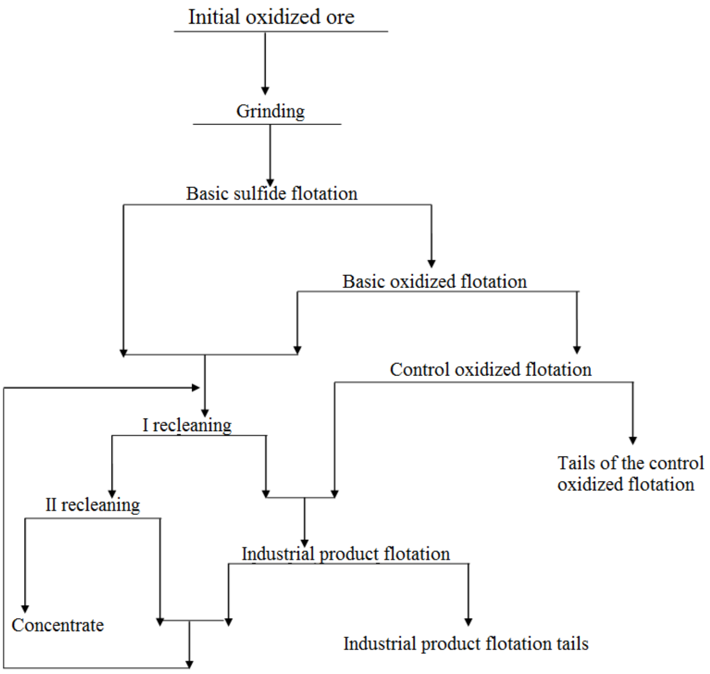

Figure 8. An improved scheme for the enrichment of copper oxidized ore from the Zharyktas deposit

Note – compiled by the authors

Table 4. Distribution of copper by products of the circuit experience

Product name	Exit, %	copper content, %	extraction of copper, %
Concentrate	1,52	21,20	65,73
Industrial product flotation tails	6,88	0,71	9,98
Tails of the control oxidized flotation	91,60	0,13	24,29
∑ tails	98,48	0,171	34,27
ore	100,00	0,490	100,00
Note - compiled by the authors			

When processing ore according to this scheme, a concentrate was obtained with a copper content of 21.20% and final tailings with a content of 0.171%, with the extraction of copper 65.73% and 34.27% of the ore, respectively.

Conclusions. Thus, the technology of processing oxidized copper ore from the Zharyktas deposit has been improved in order to increase copper extraction due to sulfidization of oxidized copper minerals. When processing this ore using an improved technology, a concentrate with a copper content of 21.20% was obtained, which increased copper extraction by 42.77% compared to the basic technology. The improvement of the technology for processing oxidized copper ore from the Zharyktas deposit and its successful implementation into production in the future will increase the efficiency of ore processing and obtain a technical and economic effect.

Conflict of interest. The author(s) declare that there is no conflict of interest.

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