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BENEFICIATION OF SULFIDE ORE FROM A PORPHYRY-COPPER DEPOSIT

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Abstract

The presentation that is summarized in this article focused on the results obtained from laboratory studies carried out for beneficiation of primary sulfide ores from porphyry - copper deposit. To determine the primary sulphide ore physical composition, full chemical analysis and X-ray diffraction analysis, phase analysis, study through polarizing microscope in reflected light of polished ore samples were carried out. The sulfide copper ore particle size composition and grindability were studied. The technological studies result shown that selective-bulk flotation flowsheet developed, with copper and pyrite concentrate production is effective for the sulfide copper ore. Finally, conclusions and summaries are presented.

Keywords: *beneficiation, primary sulfide ore, porphyry - copper deposit, flotation*

1. INTRODUCTION

Copper is one of seventeen elements defined by the European Union as "critical" - economically and strategically important for the European economy, for realize a low-carbon future. According to Harrington [Nature World Bank Report 2020], copper consumption is expected to increase seven times by 2050 (compared to 2018). In nature, copper is most often found in the following minerals: chalcopyrite, chalcocite, bornite, covellite, malachite, azurite, chrysocolla, cuprite, tenorite, etc.

Porphyry-copper deposits represent an important, dominant source of metal copper, which provides about 75% of the world's copper production, and significant amount of molybdenum and gold. Furthermore, rhenium, silver, selenium, tellurium, etc. are also obtained from them as byproducts [Tsekov et al., 2003], [Sillitoe, 2010], [Angelov et al., 2013], [John, Taylor, 2016]. About 50% of the world's copper is mined from porphyry deposits, and the remaining amount is mainly mined from vein type deposits [Mochev, Grigorova 2015].

Porphyry-copper deposits are most often characterized by large sizes and a large amount of reserves (from the order of 100 million to several billion tons), with poor mineralization and primary ores low metal content – Cu (0.2 – 1.5%), Mo (< 0.01 – 0.3), Au (<0.01 – 1 g/t), [Dilles, John, 2021], [Yankova, Angelov, Nishkov, 2021].

As mentioned by Grigorova [Grigorova, 2020], the heterogeneous nature of the rock varieties complicates the mining process, creating difficulties mainly in the ore comminution. To study the operational porphyry-copper deposits characteristics and the rock varieties detailed mapping, it is appropriate to apply geophysical methods based on the difference composition in the minerals physical properties and the rocks containing them. Despite the metals low content, due to deposits large size, a few valuable components presence and mining carried out by open-pit method, the porphyry-copper deposits exploitation is economically the most effective [Yankova, Angelov, Nishkov, 2021].

Copper ores are characterized by multiple minerals being economically viable to mine. Many of them can occur in the same deposit in different proportions and depths. This fact made their examination and exploration extremely difficult. Very useful in this stage of the research are geophysical methods and particularly electrical resistivity tomography. According to Tomova, geophysical methods are commonly used in exploration for identification and delimitation of mineral deposits and have played an important role in reducing geological uncertainty in mining [Tomova, 2023].

The great interest to porphyry-copper deposits, which for the last 40-50 years have continued to be subject of intensive and in-depth scientific research and geological studies, is primarily explained by the fact that they contain large copper and copper-molybdenum reserves, suitable for open pit mining, which determines their primary importance in copper and molybdenum mining [Bogdanov, 1987].

In recent decades, the world mining of non-ferrous metal ores development has been characterized by increasingly poor deposits. Deposits with a relatively low content of non-ferrous metals are exploited, whose ores, however, due to the large extents and capacities are developed at higher productivity and relatively reduced costs, and they can only be processed in large beneficiation factories. Nowadays, non-ferrous metals are produced from such deposits very often, more cheaply, than from high-metal vein deposits. Along with the rapidly progressing mining technique and the modern beneficiation technique has a decisive part.

As early as 2010, Norgate and Jahanshahi [Norgate, Jahanshahi, 2010] reported that the metal content of ore is declining globally, as higher quality reserves are exploited first and gradually depleted. At the same time, demand for base metals derived from these ores is expected to grow, despite increased recycling rates.

The level to which processing technologies for poor copper ores from sulphide deposits have reached by 2020 is expressed of Jinghe Chen et al. [Jinghe Chen, Xian Jian Guo, Hongxu Li, 2020]: "To copper recovery from low-grade sulfide ore in an environmentally sustainable manner is a real challenge."

Due to the depletion of high-quality porphyry-copper sulfide ore deposits, the focus of mineral processing researchers has shifted to the development of new, highly efficient and environmentally friendly technologies for beneficiation of primary sulfide ores from porphyry-copper deposits.

Research and development program of Department of Mineral Processing and Recycling, University of Mining and Geology "St. Ivan Rilski" has started to establish the technological possibilities for beneficiation of primary sulphide ores from porphyry-copper deposit in Bulgaria. The technological research aims to develop a technology for copper and pyrite recovery in separate concentrates from the sulphide copper ores from the porphyry-copper deposit.

2. MATERIALS AND METHODS

2.1. Materials

The experimental laboratory tests were carried out with ore sample weighing more than 300 kg. The sample was crushed using jaw crusher, roll crusher and impact crusher to required size. The particle size analysis was performed with a laboratory vibratory sieve machine Analysete 3, using laboratory sieves set with sieve surfaces opening sizes: 2.5 mm, 1.25 mm, 0.500 mm, 0.250 mm, 0.125 mm, 0.080 mm. In order to determine the dependence between grinding duration and milled product size, experiments were carried out at grinding time: 4, 7, 10, 12, 15, 20 and 25 minutes. The Bond work index determination was performed using a standard Bond mill with dimensions D x L = 305x305 mm; mill volume 22.3 dm^3; smooth steel liners; rotation speed 70 min^{-1}; grinding medium - steel spheres with a total mass of 22.544 kg.

Having in mind the material composition and technological sample physico-mechanical properties, as well as the trends in the world practice of poor copper porphyry ores beneficiation, a selective-bulk flotation flowsheet was adopted.

2.2. Methods

To determine the studied ore material composition, the following laboratory tests were carried out: full chemical analysis and X-ray diffraction analysis, study through an polarizing microscope in reflected light of porphyry copper ore polished sections. A phase analysis was carried out to determine the forms of presence of copper in ore: water-soluble copper, oxidized free and bound copper, primary and secondary copper sulfides.

Studies on the grain size characteristics were performed and to determine the ore grindability, as well as to study valuable minerals liberation degree, depending on milling duration. The Bond Energy Index was calculated.

It was developed three cycles flotation flowsheet includes: bulk flotation, copper-pyrite selection and pyrite flotation. Flowsheets and technological regimes for individual cycles are independently determined.

The bulk flotation main parameters, having a significant influence on the technological indicators, were studied through a series of laboratory experiments. With studied parameters established optimal values, experiments were conducted in a closed circuit to determine the bulk flotation technological indicators. Mineral processing flowsheet and technological regime have been developed to determine the technological indicators of copper-pyrite selection and pyrite flotation of sulfide ore.

In this study, to determine the rougher flotation optimal conditions, for sulphide copper ores beneficiation was used one of the most accurate methods in the mineral processing research practice, namely the factorial method of experiments planning, proposed by American chemists Box and Wilson.

3. RESULTS AND DISCUSSION

3.1. Porphyry-copper ore chemical analysis and copper phase analysis

Table 1 presents the results of porphyry-copper ore chemical analysis and table 2 shows the phase distribution of copper in porphyry-copper ore.

Table 1. Porphyry-copper ore chemical analysis

Components	Content, %	Components	Content, %
Cu	0.215	**Al_2O_3**	13.85
Mo	0.0041	**Fe_2O_3**	4.96
Au (g/t)	0.06	**CaO**	4.65
Zn	0.0040	**MgO**	1.21
Pb	0.0020	**MnO**	0.09
As	0.0003	**Na_2O**	2.44
Sb	0.0006	**K_2O**	3.69
S	0.83	**TiO_2**	0.48
C	0.10	**P_2O_5**	0.26
SiO_2	62.98		

The data from chemical analyzes (Table 1) reports that the copper content (Cu) in ore is 0.215%, molybdenum (Mo) – 0.0041% and gold (Au) 0.06 g/t. Increased contents of SiO_2, Al_2O_3, Fe_2O_3, CaO, K_2O, etc., whose carriers are the non-ore phases accompanying ore sulphide mineralization, are found in ore.

Table 2. Phase distribution of copper in porphyry-copper ore

Form of the compound	Content, %	Distribution, %
Cu soluble in water	0.001	0.44
Oxide free Cu	0.004	1.79
Oxide Cu bonded	0.004	1.79

Cu soluble in cyanides	0.035	15.62
Cu, insoluble in the above solvents	0.180	80.36
Total Cu	0.224	100.00

Phase analysis results (Table 2) indicate that the main part of copper - 80.36% is represented by primary sulfide minerals (chalcopyrite) and to a lesser extent by secondary copper sulfides - 15.62%. The copper oxide content (3.6%) and water-soluble copper (0.44%) is relatively low.

The data from X-ray structural analysis (Fig. 1), carried out to determine the ore sample mineral composition, demonstrates that in quantitative terms non-ore phases predominate sharply (93%). The ore phases (about 6%) are represented by magnetite (3%), pyrite (2%) and chalcopyrite (1%). Quartz (42%), followed by muscovite (14%), feldspars - albite (12%) and microcline (9%), chlorite - clinochlore (9%), pyroxene - diopside (5%). Non-ore phases accompanying sulphide mineralization are predominantly quartz and rarely calcite (1%) and barite (1%). Ore minerals are represented by magnetite (3%), pyrite (2%) and chalcopyrite (1%).

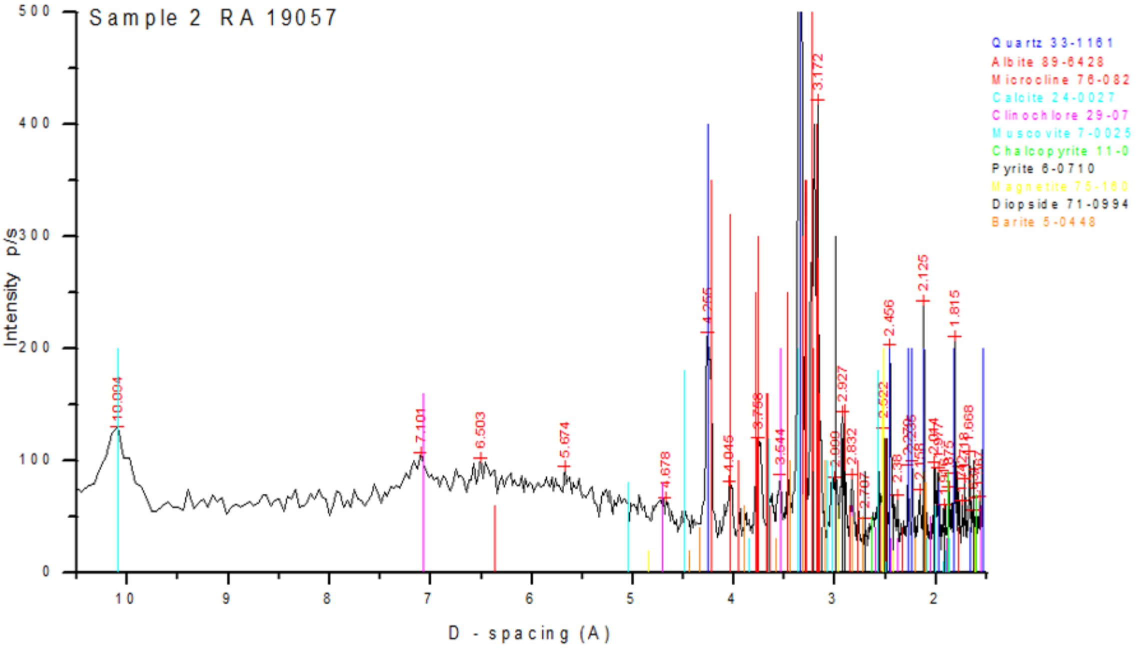

Fig. 1. X-ray structural analysis of porphyry-copper ore technological sample

3.2. Mineralogical studies

Mineralogical studies were carried out on three types of ore samples with a visually sulphide mineralization higher content. In first samples type pyrite is the main, quantitatively predominant ore mineral. Compared to pyrite, chalcopyrite is observed in a smaller amount. Bornite and coveline occur rarely, in close association with chalcopyrite. In second type, the total ore minerals amount is about 2-3%. Ore minerals are mainly represented by pyrite, chalcopyrite and magnetite.

In third type ore minerals are mainly represented by pyrite, chalcopyrite and magnetite. A minimal amount of hematite was found. Triple intergrowths of pyrite-chalcopyrite-nonmetal minerals occur in a minimal amount. Compared to pyrite and magnetite, chalcopyrite is less abundant.

3.3. Ore grindability research

The obtained results from ore grindability research are presented in figure 2 and figure 3. It was found that to obtain 65% size fraction - 0.080 mm, a grinding duration of 11 minutes was required (Figure 4)

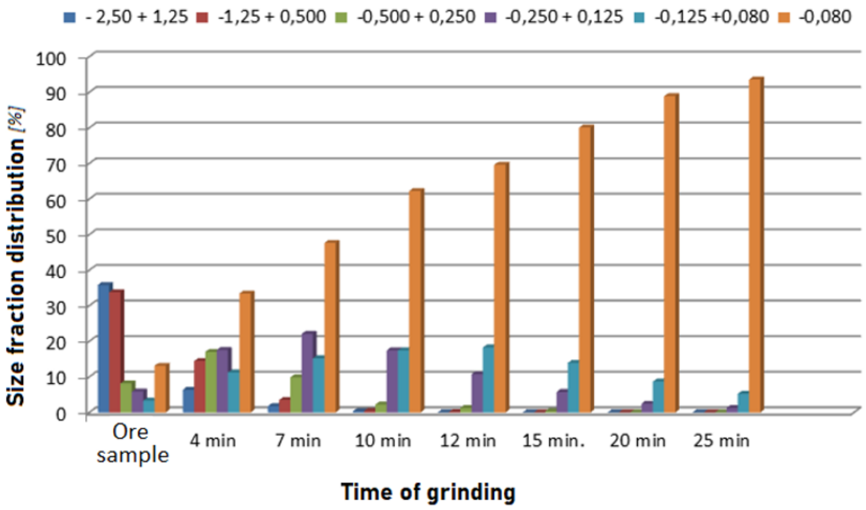

Fig. 2. Particle size distribution at different grinding duration

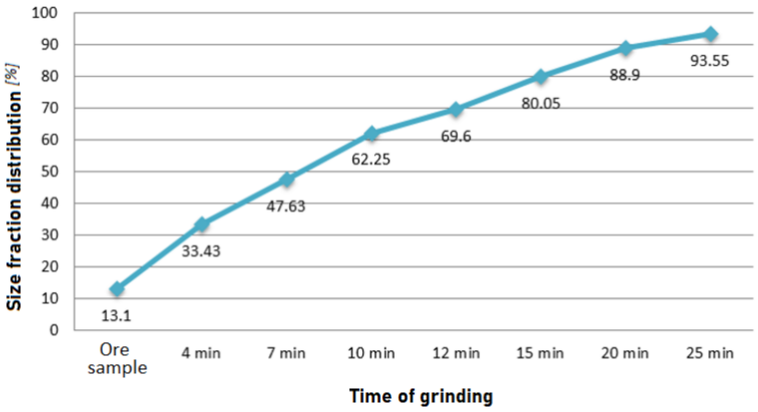

Fig. 3. Size fraction distribution “-0.080 mm”, depending on grinding duration

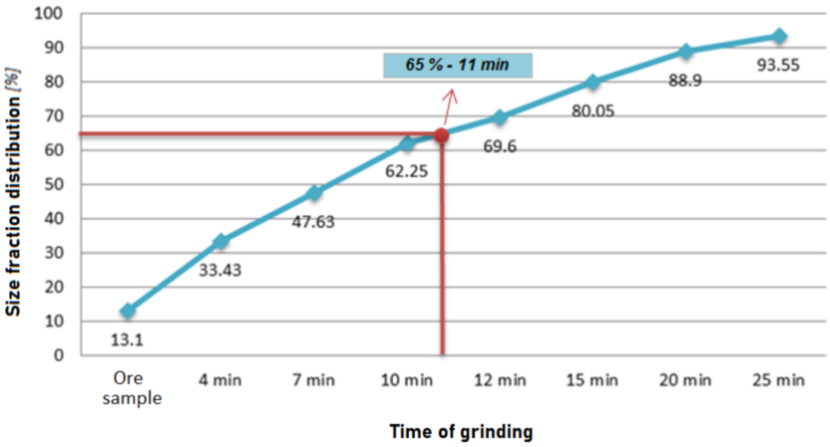

Fig. 4. Determination of grinding time for 65% size fraction “-0.080 mm”

3.4. Bond Energy Index determination

Bond Work Index is the most widely used parameter to measure the rock and ore grindability. Bond Ball Mill Index (BMWi) test is an industry standard for determining the Bond Work Index of ore sample under ball milling conditions. The Bond Work Index is used to ball milling process energy requirements (kWh/t) determine for:

- New equipment and grinding circuits design;
- Optimization of existing ball mill circuits to maximize throughput and/or minimize power usage;
- Ore body characterization, etc. [Grigorova, Ranchev, 2019].

In the laboratory tests, Bond Work Index value was determined by a grindability test in a standard Bond ball mill, in 9 grinding cycles. The main test parameters were:

- Control (calculation) sieve Pc = 0.100 mm;
- Sample for grinding M = 1073 g;
- Fraction -Pc + 0 in the grinding sample f = 8% = 0.08;

Approximate undersieve product mass (calculated): C = 306.57 g with a circulating load 250%. C = M/3.5. Ore grindability test data required to calculate the Bond Work Index (W_i): $P_c = 100$ µm; G = 1.61 g; $F_{80} = 2.17$ mm; $P_{80} = 78$ µm. The calculated Bond Work Index (Wi): 13.9 kWh/t. The energy consumption for 1 g of newly formed fraction: W_G is 6.65×10^{-3} kWh/g.

The ore grindability results and determined Bond Work Index shown that the sulphide ore is easily for grinding.

3.5. Flotation studies

In this report, to determine the rougher flotation optimal conditions, for sulphide copper ores beneficiation, has been used the factorial method of experiments planning. In this method, a certain number of levels (values) are selected for each factor, after which all possible combinations are implemented, thus realizing a complete factorial experiment [Draper, N.R 1992].

The optimal conditions of basic rougher flotation were determined by Box and Wilson's for experiment multifactorial design. The following variable factors were investigated: X1 – grinding degree, % fraction "-0.08 mm"; X2 – regent regulator consumption – lime, g/t; X3 - regent collector consumption - mixture of isobutyl and isoamyl xanthogenate (1:1) and Hostaflot, g/t; X4 - frother - OrePrep X-133, g/t; X5 – flotation time, min. The copper and sulfur recovery in the concentrate from rougher flotation were taken as optimization parameters.

Based on the data received, the following conditions were considered optimal: grinding degree -65 % fraction "-0.08 mm", CaO consumption - 450 g/t, collectors' consumption - 30 g/t, frother consumption OrePrep X-133 - 9 g/t and flotation time 11 min.

The experiments were carried out according to flowsheet shown in Figure 5. Table 3 illustrates the planning matrix, the results of the parallel trials, and the objective functions average values.

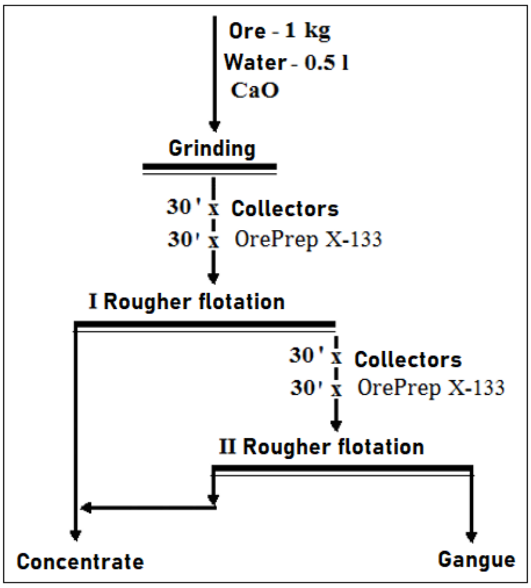

Fig. 5. Flowsheet of experiments to rougher flotation optimal conditions determine

Table 3. Planning matrix and experiments results on multifactorial planning to determine rougher flotation optimal conditions

Variables factors	**Indicators**	**Variables factors**					**Objective function**					
		X_1	X_2	X_3	X_4	X_5	€$_{Cu1}$	€$_{Cu2}$	€$_{Cu}$	€$_{S1}$	€$_{S2}$	€$_{S}$
X1 – grinding degree, % fraction "-0.08 mm"	Basic level	65	450	30	5	3						
	Step of variation	5	150	5	2	2						
X2 – regent regulator consumption – lime, g/t;	Upper Level /+/	70	600	35	7	10						
	Bottom level /-/	60	300	25	3	6						
X3 - regent collector consumption - mixture of isobutyl and isoamyl xanthogenate (1:1) and Hostaflot, g/t	Experiment number: 1	-	-	-	-	-	85.45	83.57	84.51	64.85	61.58	63.22
	2	+	+	-	-	-	80.70	90.02	85.36	78.00	85.12	81.56
X4 - frother - OrePrep X-133, g/t	3	-	-	+	+	-	90.85	81.11	85.98	88.67	67.50	78.09
	4	+	-	+	-	+	88.51	91.65	90.08	80.97	84.96	82.97
	5	-	+	+	-	+	86.10	87.20	86.65	80.15	80.03	80.09
X5 – flotation time, min	6	+	-	-	+	+	86.88	84.01	85.44	85.01	87.05	86.03
	7	-	+	-	+	+	91.15	93.20	92.17	89.71	91.02	90.36
	8	+	+	+	+	-	90.13	93.20	91.66	91.42	79.98	85.70
	Basic level	65	450	30	5	8	91.59	91.02	91.30	89.99	87.90	88.94

As a result of experimental study conducted, it was established that in the studied interval of copper recovery factors, all parameters are insignificant. It was found that for sulfur recovery from rougher flotation, frother consumption and flotation time have a significant effect.

To bulk copper-pyrite (Cu-Py) flotation technological parameters determine, experiments in closed cycle were carried out.

Based on the results obtained, the following values of the technological parameters can be accepted as optimal for bulk cycle:

- Grinding – 0.65 % fraction "-0.08 mm";
- Modifying flotation reagent (CaO) consumption - pH-9 – 450 g/t;
- Reagent collector (mixture of isobutyl and isoamyl xanthogenate 1:1 and Hostaflot) consumption – 30 g/t;
- Reagent frother consumption: OrePrep X-133 – 9 g/t;
- Bulk flotation duration – 10-12 min;
- Cleaner flotation duration - 5 min;
- Control of cleaner flotation duration - 5 min;
- Kerosene consumption in bulk flotation – 30 g/t.

To study the products material composition, from bulk flotation cycle, chemical, particle size and mineralogical analyzes were carried out. Particle size analysis shows that copper and sulfur losses are concentrated in the "+ 0.125 mm" fraction (31% copper and about 33% sulfur losses). Mineralogical analysis highlights that these losses are due to fine intergrowths of sulphides with non-ore minerals.

Obtained results from the research conducted could be summarized:

After bulk flotation concentrate grinding to 85% fraction "-0.08 mm", a residual CaO concentration respectively in copper-molybdenum flotation 500-550 g/m^3 and in first cleaner flotation 700 g/m^3, a copper concentrate with a copper content of 20.2% and copper recovery 98.3% in the selection cycle have been received. When grinding the bulk flotation concentrate to 95% fraction "-0.08 mm" and residual free CaO concentration in copper-molybdenum flotation 700 - 750 g/m^3, in the first cleaner flotation 850 - 900 g/m^3, a copper concentrate containing 21.3% and copper recovery is 97.2% in selection cycle are obtained.

The obtained copper concentrates have an average copper content of 20.8% and sulfur 25.1% (chalcopyrite – 60%, pyrite – 8% and non-ore minerals – 32%). Copper concentrate contamination is mainly due to fine intergrowths of chalcopyrite and pyrite with rock-forming minerals (in "+0.08 mm" fraction). Copper losses in the tailings are due to fine intergrowths between chalcopyrite and rock-forming minerals and to slimes in the fine fractions. The molybdenum content in the copper concentrate is 0.35%. Molybdenum recovery from the flotation cycle is satisfactory: 88.5 – 89.9 %.

As a result of recent review of the literature on this topic, the possibility of obtaining pyrite concentrate from sulphide ores from pyrite flotation cycle high extraction has been established.

Based on the technological studies conducted, to determine the beneficiation of sulphide copper ores from a porphyry-copper deposit has been developed a selective-bulk flotation flowsheet for copper and pyrite concentrates obtaining (fig. 6).

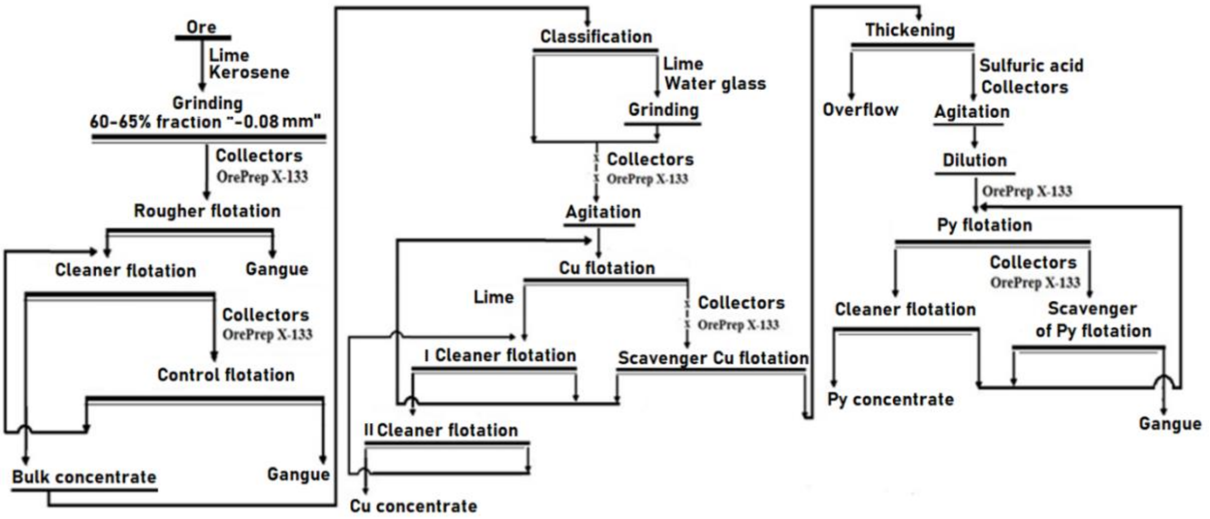

Fig. 6. Selective-bulk flotation flowsheet and primary sulphide ores technological beneficiation regime

The technological flotation studies prove that the developed selective-bulk flotation flowsheet with copper and pyrite concentrates production is rational for primary sulfide ores in the porphyry-copper deposit. According to the selective-bulk flotation flowsheet, presented on the figure 6, in laboratory conditions, the following products were obtained: copper concentrate - 21.3% Cu, 25% sulfur and 0.33% molybdenum with copper recovery 88.17%, sulfur - 26.8% and molybdenum 73.4%. Pyrite concentrate contains 50.2% S, when extracted from total sulfur is 66.5%.

Table 4 summarizes the primary sulfide ores technological studies data and results.

Table 4. Primary sulphide ores beneficiation results

Products	Yield, %	Grade, %			Recovery, %		
		Copper	Sulphur	Molybdenum	Copper	Sulphur	Molybdenum
Copper concentrate	0.89	21.3	25.0	0.33	88.17	26.81	73.42
Pyrite concentrate	1.10	0.16	50.2	0.013	0.82	66.53	3.58
Gangue	98.01	0.024	0.056	0.0009	11.01	6.66	23.00
Ore	100.00	0.215	0.83	0.004	100.00	100.00	100.00

4. CONCLUSIONS

A complex technological study was carried out for beneficiation of primary sulphide ore from a porphyry-copper deposit, to copper concentrate obtain. The sulphide ore beneficiation has been proven, by flotation method for processing. The chemical, mineral and particle size composition, as well as the grindability of the primary sulphide copper ore, were studied and analyzed.

The technological ore sample characterizes the primary sulphide copper ore. The main valuable component in the ore is copper – 0.215%. Sulfur - 0.83 % and molybdenum - 0.0041 % were found as accompanying valuable components with industrial importance. Copper in ore sample is represented by chalcopyrite (80% relative to total copper), secondary copper sulfides (15.6% relative to total copper) and oxide copper minerals (3.6% relative to total copper).

Copper is mainly concentrated in "-0.080 mm" fraction, sulfur in "-0.20+0.04 mm" fraction. Molybdenum is relatively evenly distributed in fractions below 0.200 mm. It was found that P65 "–0.080 mm" is the optimal grinding degree for sulfide ore. The chalcopyrite is almost completely (90%) liberated at size "-0.125 mm". The same goes for pyrite. Molybdenite is fully revealed at grain sizes below 0.080 mm.

Selective-bulk flotation flowsheet was developed, including three cycles - bulk flotation, copper-pyrite and pyrite flotation, and the optimal technological parameters for each separate flotation cycle were experimentally determined.

The results presented in this work extend our knowledge of primary sulphide ores from porphyry-copper deposit beneficiation.

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