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Investigation of Copper Ores Processing Products

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Abstract: In recent years, the world technics and technologies development in mineral beneficiation has shown significant achievements in the field of mineral separation basic phenomena and regularities. This allows for creation of highly efficient processes and technologies for processing of primary ore with a complex composition, thus providing the metallurgical industry with necessary high-quality concentrates. As well known, the concentrates produced by beneficiation plants are subject to certain requirements for content of valuable components and harmful impurities. In order concentrates to be a commodity product, they must contain valuable components more than minimum permissible content, and harmful impurities must be a lower content than the maximum permissible. The presentation that is summarized in this article focuses on the results of laboratory experimental studies conducted to characterize copper, pyrite and molybdenum concentrates obtained from sulphide copper ores processing. This study also explored copper and pyrite concentrates from sulphide-oxide copper ores and oxide ores productive solutions. Data from concentrates chemical and particle size analysis are presented. Moreover, a brief description of technological studies conducted, their aims, concentrates and productive solutions obtained are presented. All copper concentrates contain gold and silver, as accompanying valuable components. Harmful impurities other than carbon in the molybdenum concentrate have not been detected. We summarize that all copper products are suitable for copper concentrates market.

Keywords: Characterization, Concentrates, Sulphide copper ores

Introduction

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 makes their examination and exploration extremely difficult. Many experts contend the present stage of mineral-raw material industry evolution is describing by mineral deposits with complex mining-geological conditions, difficult for mining, low grade ores with complex processing, which leads to considerable waste quantities formation (Tomova, 2023).

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 et al., 2021).

The exceptional interest in porphyry-copper deposits, which for the last years have continued to be the 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 ores reserves, suitable for open-pit mining, which determines their primary importance in copper and molybdenum mining. As well known the copper sulfide ores must be concentrated before they can be economically transported and smelted. According to Schlesinger & Davenport (2011), the universal technique for concentration is froth flotation (Schlesinger & Davenport, 2011). For copper beneficiation, flotation is the most conventional method that has been used since 1905 (Jena et al., 2022). Flotation, in fact, has allowed mining of the lean and complex ore bodies that would have otherwise been discarded as noneconomic overburdens (Fuerstenau et al., 2007).

Copper concentrates typically contain around 30% of copper, but grades can range from 20 to above 40 per cent. International Copper Study Group reports that the copper concentrate can be processed pyrometallurgically in a smelter to produce matte or hydrometallurgically (pressure leaching) to produce pregnant leach solution, both products requiring further processing to copper metal obtain. In the hydrometallurgical route, copper is extracted from mainly low-grade oxide ores and some sulphide ores, through leaching (solvent extraction) and electrowinning (SX-EW process), (Assofermet, 2023). According to International Copper Study Group copper ores demand and copper concentrates production will undoubtedly continue to grow worldwide. Electric vehicles contain approximately four times more copper than conventional cars (Assofermet, 2023).

Detailed study of estimating copper concentrates benchmark prices under dynamic market conditions by Díaz-Borrego et al., (2021) showed that copper concentrates are traded globally between mines, traders and smelters, constituting the current main source of refined copper (Borrego et al., 2021). Concentrates are produced from copper sulphide ores, occurring naturally in different kinds of deposits, being porphyry deposits the most relevant ones (Borrego et al., 2021). Molybdenum and copper sulphide concentrates are the main source for obtaining one of the most expensive and rare metals of strategic importance - rhenium, which is irreplaceably used in aerospace technologies.

Therefore, searching, validating and developing effective beneficiation technologies for copper recovery is a research focus for many scientists. Due to the depletion of high-grade copper sulphide deposits, the research interest has directed to copper oxide and mixed ore deposits recovery. The aim of this paper is to reports the results of characterize copper, pyrite and molybdenum concentrates obtained from sulphide copper ores processing, sulphide-oxide copper ores and oxide ores, in order to produce saleable concentrates quality.

This article primarily includes the following elements: study of copper, pyrite and molybdenum concentrates from sulphide copper ore processing, study of copper and pyrite concentrates from sulphide-oxide copper ores processing and oxide ores productive solutions obtaining.

Study of Copper, Pyrite and Molybdenum Concentrates from Sulphide Copper Ore Processing

Research and development program has started to establish the technological possibilities for beneficiation of sulfide, sulphide-oxide and oxide copper ores from porphyry-copper deposit in Bulgaria. The technological research aims to develop a technology for copper, pyrite and molybdenum recovery in separate concentrates from the sulphide copper ores.

Copper and Pyrite Concentrate from Sulphide Copper Ores

Technological investigations have been conducted for processing of primary sulphide copper ore from a porphyry-copper deposit (Yankova & Grigorova, 2022). The chemical, mineral and particle size composition, as well as the grindability were studied and analyzed. For copper presence forms determining the phase analysis has been performed. 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 (Yankova, et al., 2021). The gold content is 0.06 g/t. Copper in the 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).

The sulphide ore beneficiation has been proven by flotation. A selective-bulk flotation flowsheet has been developed, including three cycles - selective flotation, copper-pyrite flotation and pyrite flotation, and the optimal technological parameters for each individual flotation cycle have been experimentally determined. The selective-bulk flotation flowsheet includes the following operations: ore grinding to 65% fraction "- 0.080 mm"; rougher, cleaner and scavenger flotation; Cu-Py concentrate grinding to 95% fraction "- 0.080 mm"; rougher and scavenger copper-molybdenum flotation; two consecutive cleaner flotation to copper concentrate obtain; copper flotation waste thickening, agitation and dilution; rougher and scavenger pyrite flotation; cleaner flotation to pyrite concentrate obtain.

The results of technological investigations conducted show that the developed selective-bulk flotation flowsheet, with obtaining copper and pyrite concentrate is effective for sulphide copper ores. The technological studies prove that the developed selective-bulk flotation flowsheet with copper and pyrite concentrates production is rational for sulphide ores. According to selective-bulk flotation flowsheet, the following final products and technological indicators were obtained: copper concentrate containing 21.3% copper, 25% sulphur, 0.33% molybdenum and 4.58 g/t gold with copper recovery 88.17%, sulfur - 26.81%, molybdenum 73.4% and gold 69.42%; pyrite concentrate containing 50.2% sulfur, recovery from the total sulfur is 66.5%. Table 1 presents the data from copper concentrate chemical analysis and Table 2 illustrated the data from a particle size analysis with valuable components distribution by fraction for copper concentrate.

Table 1. Copper concentrate chemical composition

Product	Cu, %	Mo, g/t	Au, g/t	S, %	C, %	Na_2O, %	MgO, %	LoI, %
Cu concentrate	21.38	31.00	4.68	25.05	0.42	0.49	0.11	2.03
	Al_2O_3, %	SiO_2, %	P_2O_5, %	K_2O, %	CaO, %	TiO_2, %	Fe_2O_3, %	
	4.19	5.48	0.43	0.50	0.90	0.19	28.04	

Table 2. Particle size analysis with distribution of valuable components by fraction for copper concentrate

Particle size fraction, mm	Yield, %		Grade, %			Recovery, %		
	Mass pull	Cumulative	Cu	S	Mo	Cu	S	Mo
+0.080	7.10	7.10	11.78	17.71	0.199	3.91	5.01	4.72
-0.080 +0.040	31.92	39.02	20.12	25.30	0.310	30.01	32.18	33.03
-0.040 +0.025	20.70	59.72	22.99	26.07	0.379	22.15	21.50	26.15
-0.025 +0.010	19.10	78.82	26.83	28.28	0.038	23.95	21.52	24.10
-0.010	21.18	100.00	20.19	23.45	0.170	19.98	19.79	12.00
Total	100.00	-	21.40	25.10	0.30	100.00	100.00	100.00

Table 3 presents the data from pyrite concentrate chemical analysis and Table 4 illustrated the data from a particle size analysis with distribution of valuable components by fraction for pyrite concentrate.

Table 3. Pyrite concentrate chemical composition

Product	Cu, %	Mo, g/t	Au, g/t	S, %	C, %	Na_2O, %	MgO, %	Al_2O_3, %
Py concentrate	0.17	130	-	50.50	-	0.27	0.04	2.50
	SiO_2, %	P_2O_5, %	K_2O, %	CaO, %	TiO_2, %	Fe_2O_3, %	LoI, %	
	3.10	0.25	0.13	0.20	0.66	71.80	-	

Table 4. Particle size analysis with distribution of valuable components by fraction for pyrite concentrate

Particle size fraction, mm	Yield, %		Grade, %			Recovery, %		
	Mass pull	Cumulative	Cu	S	Mo	Cu	S	Mo
+0.080	22.10	22.10	0.157	42.80	0.005	20.10	18.68	8.30
-0.080 +0.040	42.50	64.60	0.147	53.04	0.008	36.15	44.53	24.15
-0.040 +0.025	19.01	83.61	0.137	52.80	0.014	15.10	19.83	20.10
-0.025 +0.010	8.30	91.91	0.27	52.97	0.036	13.15	8.69	22.03
-0.010	9.09	100.00	0.33	51.74	0.042	15.50	8.27	25.42
Total	100.00	-	0.173	50.62	0.0135	100.00	100.00	100.00

Molybdenum Product from Sulphide Copper Ores

This research study was conducted to illustrate the possibility to obtained molybdenum concentrate from sulphide copper ores. The molybdenite, which accounts for over 90% of the world's molybdenum production, is usually associated with sulfide minerals of other metals, mainly copper. The molybdenum content in ores varies from 0.01 to 0.5%, and in copper-molybdenum sulfide ores it is 0.01-0.05% and reaches 0.12-0.5% in molybdenum sulfide ores. Sulphide molybdenum ores are less common, but due to their large reserves and fact that their molybdenum content is many times higher than in copper-molybdenum ores are important. The molybdenum production from these ores is main activity, and most often the total production costs are covered entirely by the obtained molybdenum concentrate, as opposed to copper-molybdenum ores processing (Kovacheva, 2009).

With steel growth, oil and gas industries and need for corrosion-resistant alloys, the main users of molybdenum, molybdenum-rich ores are being depleted. Molybdenum ores search is a complex process due to the specific conditions of their formation and deposition. Molybdenum ores are extremely unfavorable for direct geological-gephysical prospecting and exploration. With some success, it is possible to apply electrotomography - a method based on the study of the geoelectric section of the studied area, and its geological effectiveness is determined by the differentiation of the environment by specific electrical resistance (Grigorova, 2020). This requires researchers efforts to be directed to study the possibilities for full molybdenum recovery from poor molybdenum-containing ores. Technological investigations were carried out for beneficiation of primary sulphide ore from a porphyry-copper deposit to molybdenum concentrate obtain. The chemical, mineral and particle size composition as well as sulphide copper ore grindability were studied. Phase analysis for copper presence forms determining has been performed.

Selective-bulk flotation flowsheet was developed, including three cycles: bulk flotation, copper-pyrite selection and pyrite flotation, and the optimal technological parameters for each flotation cycle have been experimentally determined. The copper-molybdenum selective-bulk flotation flowsheet includes: copper-molybdenum concentrate thickening up to 50%, conditioning, diluted to 25%, rougher molybdenum flotation and 11 molybdenum refining operations. It was found that molybdenum is represented by molybdenite, mostly associated with chalcopyrite and less frequently with pyrite. With the copper-molybdenum concentrate from the technological sample laboratory experiments were conducted, to determine the optimum values of the main factors, which have a significant effect on molybdenum flotation (Yankova, 2023). Table 5 presents the data from molybdenum concentrate chemical analysis and Table 8 illustrated the data from a particle size analysis with distribution of valuable components by fraction for molybdenum concentrate.

Table 5. Molybdenum concentrate chemical composition

Components	Contents, %	Components	Contents, %
Mo	32.0	MgO	0.38
Cu	1.85	K_2O	0.20
S	24.50	Na_2O	2.01
Fe	2.90	Re, g/t	150
SO_2	2.00	As	0.02
Al_2O_3	2.33	Sb	0.005
CaO	1.02	C	35.00

The molybdenum concentrate chemical analysis shows a significant carbon content – 35% (Table 5). The carbon presence was found in the ore technological sample composition from which copper-molybdenum concentrate was obtained. The ore carbon content was 0.1%, and in the copper-molybdenum concentrate – 0.42%. Since carbon particles have the same hydrophobicity as molybdenite, under the selection conditions of the copper-molybdenum selective-bulk flotation they are extracted together in the molybdenum concentrate.

Based on the chemical analysis, the following minerals composition in the 32 % molybdenum concentrate was calculated: molybdenite - 53.3%, chalcopyrite - 5.3%, pyrite - 2.5%, non-ore minerals 10.9% and 38% carbon products. The obtained results show that copper-molybdenum concentrate selection is performed at a relatively low efficiency. From the molybdenum concentrate particle size analysis presented on the table 6 can be seen that impurities of non-ore minerals and carbon products are concentrated in coarse classes (+0.08 mm).

From the investigated technological ore sample, the highest indicators were obtained when a mixture of sodium sulfide and sodium hydrosulfide in a ratio of 1:1 was used, as a depressant of copper minerals and pyrite. The final molybdenum product obtained contains 32% molybdenum, and its recovery in an open cycle from the collective concentrate is 64%, and from the ore – 46.7%.

Table 6. Particle size analysis with distribution of valuable components by fraction for molybdenum concentrate

Particle size fraction, mm	Yield, %		Grade, %			Recovery, %		
	Mass pull	Cumulative	Mo	Cu	S	Mo	Cu	S
+0.080	14.40	14.40	5.18	0.77	7.96	3.05	5.80	5.57
-0.080 +0.040	30.25	44.65	28.36	0.85	19.97	35.02	13.50	29.36
-0.040 +0.025	17.40	62.05	39.58	0.98	23.31	28.11	8.96	19.71
-0.025	37.95	100.00	21.83	3.63	24.60	33.82	71.74	45.36
Total	100.00	-	25.50	1.90	20.58	100.00	100.00	100.00

Study of Copper and Pyrite Concentrates from Sulphide-Oxide Copper Ores Processing

İn this section we discused the technological possibilities for beneficiation of sulphide-oxide copper ores from porphyry-copper deposit in Bulgaria. The technological research aims to develop a technology for copper and pyrite recovery in separate concentrates. The laboratory test work started to establish the sulfide-oxide ore beneficiation opportunity and high-quality concentrates obtaining. The research carried out includes full chemical analysis, phase analysis for determining the forms of copper presence in the ore, X-ray diffraction analysis, mineralogical studies of polished sections from ores samples and polished briquettes, prepared from class 2.00-0 mm of the ore, studied through a polarizing microscope in reflected light. The mineral and chemical composition of the studied sulfide-oxide ore determines selective-bulk flotation application, intending to high-quality copper and pyrite concentrates obtain (Yankova, 2023).

Laboratory studies to determine the sulfide-oxide ore grindability at different grinding time (5, 7, 10, 13, 17, 22 min). The ore minerals liberation degree in milled ore different fractions has been determined by microscopic studies. The copper distribution by ore fractions, ground to 65% of the fraction “0.080 mm” has been determined. A laboratory Bond test was performed, and the Bond Work Index was determined. The results of the conducted research show that the studied mixed sulfide-oxide ore is characterized by relatively easy grindability (Yankova & Grigorova, 2023).

The main valuable component in the ore is copper - 0.554%. The ore sample is characterized by a relatively high copper content compared to the samples studied and presented in previous sections. Pyrite sulfur - 1.27 % was found as an accompanying component of industrial importance. The molybdenum and gold contents in the ore are low, respectively: Mo – 0.0029 % and Au – below 0.05 g/t. Copper phase analysis shows the following copper minerals distributions: 19.78% of copper is in the form of oxidized free copper; copper in the form of secondary sulfides amounts to 23.74%; 55.40% of copper is represented by primary copper sulfides.

Obtained results from research conducted could be summarized: the technological flotation studies carried out prove that with a selective-bulk flotation flowsheet for beneficiation of mixed sulphide-oxide ores from porphyry-copper deposit high technological indicators for this ore type are achieved. The following products and parameters were obtained: copper concentrate with 24.64% copper grade, sulfur 28.20%, with 80.21% copper recovery and sulfur 40.19%, pyrite concentrate with 45.26% sulfur grade and 47.10% total sulfur recovery (Yankova et al., 2023).

Table 7 presents the data from copper concentrate chemical analysis and Table 8 illustrated the data from a particle size analysis with distribution of valuable components by fraction for copper concentrate. Table 9 presents the data from pyrite concentrate chemical analysis and Table 10 illustrated the data from a particle size analysis with distribution of valuable components by fraction for pyrite concentrate

Table 7. Copper concentrate chemical composition

Product	Cu, %	Mo, g/t	Au, g/t	S, %	C, %	Na_2O, %	MgO, %	
Cu concentrate	24.65	844	0.54	28.30	0.21	0.65	0.45	
	Al_2O_3, %	SiO_2, %	P_2O_5, %	K_2O, %	CaO, %	TiO_2, %	Fe_2O_3, %	LoI, %
	6.52	10.65	0.39	1.40	0.72	0.18	34.48	1.82

Table 8. Particle size analysis with distribution of valuable components by fraction for copper concentrate

Particle size fraction, mm	Yield, %		Grade, %		Recovery, %	
	Mass pull	Cumulative	Cu	S	Cu	S
+0.10	7.20	7.20	10.96	28.70	3.18	7.31
-0.10 + 0.080	12.35	19.55	18.71	28.06	9.31	12.22
-0.08 + 0.063	20.25	39.80	16.62	28.06	13.56	20.04
-0.063 + 0.040	23.40	63.20	27.53	28.26	25.96	23.32
-0.040 + 0.025	12.20	75.40	32.18	29.47	15.82	12.68
-0.025 + 0.010	15.90	91.30	33.45	30.77	21.43	17.25
-0.010	8.70	100.00	30.64	23.40	10.74	7.18
Total	100.00	-	24.82	28.36	100.00	100.00

Table 9. Pyrite concentrate chemical composition

Product	Cu, %	Mo, g/t	Au, g/t	S, %	C, %	Na_2O, %	MgO, %	LoI, %
Py concentrate	0.27	86	-	45.20	-	0.68	0.25	-
	Al_2O_3, %	SiO_2, %	P_2O_5, %	K_2O, %	CaO, %	TiO_2, %	Fe_2O_3, %	
	6.47	6.83	0.25	0.72	0.86	0.65	55.36	

Table 10. Particle size analysis with distribution of valuable components by fraction for pyrite concentrate

Particle size fraction, mm	Yield, %		Grade, %		Recovery, %	
	Mass pull	Cumulative	Cu	S	Cu	S
+0.125	1.26	1.26	-	-	-	-
-0.125 +0.080	19.72	20.93	0.270	36.94	21.59	17.12
-0.080 +0.063	9.97	30.96	0.231	46.06	8.79	10.17
-0.063 +0.040	33.51	64.46	0.212	47.57	27.09	35.30
-0.040 +0.025	18.49	82.95	0.212	48.53	14.95	19.87
-0.025	17.05	100.00	0.424	46.46	27.58	17.54
Total	100.00	-	0.262	45.16	100.00	100.00

Oxide Ores Productive Solutions Obtaining

Oxide ore bio-hydrometallurgical beneficiation studies were carried out. The results show that copper is mainly represented by oxide copper minerals, soluble in sulfuric acid - 90% of the total copper. Oxide copper occurs in the form of medmontite, chrysocolla, malachite, tenorite and cuprite. Sulphide copper minerals and pyrite are in minor amounts. The host rocks are mainly represented by quartz and feldspars. The high content of oxide copper minerals in the technological sample predetermines sulfuric acid as the main reagent in copper leaching. Table 11 shows the productive solution chemical composition, obtained during the technological studies for copper chemical leaching from the oxide ores.

Table 11. Chemical composition of productive solution from oxide ore beneficiation

Product of leaching	Cu, mg/dm^3	Fe, mg/dm^3	Ca, mg/dm^3	Mg, mg/dm^3	Mn, mg/dm^3
Productive solutions	5319±106	82.9±8.3	566±28	45.4±4.5	15.7±1.6
	Pb, mg/dm^3	Zn, mg/dm^3	As, mg/dm^3	SO_4^{2-} mg/dm^3	Undissolved substances, mg/dm^3
	0.25±0.02	5.6±0.6	0.07±0.01	16665	<6

Conclusion

A technological flowsheet and reagent regime for sulphide copper ores beneficiation have been developed. It has been found that it is possible to quality copper concentrate obtain. The valuable components distribution by copper concentrate fractions shows that copper is mainly concentrated in "-0.080 mm" fraction with a maximum in "-0.080+0.040 mm" fraction. Technological flotation studies results show that during sulphide ores beneficiation, it is not possible to obtain flotation molybdenum concentrate, which would represent a commercial product. The main reason due to the sulphide ore specific material composition. The ore contains carbon, mostly of organic origin, which reaches over 0.4% in the copper-molybdenum concentrate. Hydrocarbon products are naturally highly hydrophobic and in copper-molybdenum selective flotation they are recovered together with molybdenite in the molybdenum concentrate and contaminate it as harmful impurities.

A technological flowsheet and reagent regime for beneficiation of mixed sulfide-oxide copper ore from a porphyry copper deposit have been developed. It has been established that it is possible to obtain a quality copper concentrate from mixed sulphide-oxide ore. In the experiments with mixed sulphide-oxide copper ore it was found that copper is concentrated mainly in "-0.063 mm" fraction. A flowsheet for oxide ore technological research for productivity solutions production has been developed. The technological regime and forecast indicators of the oxide ore leaching from a copper porphyry deposit in industrial conditions are presented.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM Journal belongs to the authors.

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