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EVALUATION OF ORGANIC CARBON SEPARATION FROM COPPER ORE BY PRE-FLOTATION

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Abstract: This paper describes possibilities of organic carbon matter separation during a pre-flotation stage in KGHM Polska Miedz, Division of Concentrators. The paper contains a survey of organic carbon removal technologies in worldwide plants as well as KGHM achievements in this field. Laboratory flotation testing results have also been described. Next, an industrial scale trial at Polkowice Concentrator has been conducted to confirm the previous laboratory results. The results have been discussed. They indicate a positive role of the pre-flotation stage on organic carbon removal using only frother as the flotation reagent.

Keywords: *flotation, carbonaceous matter, copper ore*

Introduction

The copper ore located in the for-Sudetic monocline, besides copper and silver, contains many other valuable chemical elements. The polymetallic character of the ore and produced by KGHM Polska Miedz SA flotation concentrates influences effectiveness of pyrometallurgical processes, mainly due to the presence of harmful impurities, for example lead and organic carbon (C_{org}).

The presence of shale, the source of carbonaceous matter in the ore, has also a negative effect on flotation and pyrometallurgical processes. The presence of clay minerals and organic carbon in shale makes the production of high quality flotation concentrates, without excessive loss of copper and other metals in the flotation tailing, difficult. The reason for the diminished concentrate quality is reporting of the shale particles into the concentrate leading to an increased yield and reduced concentrate quality. Therefore, the concentrate quality, represented by the copper content, is of great significance.

On the basis of technological indices it is possible to show that the increased amount of shale in the flotation concentrate leads to a decrease of beneficiation efficiency. This also leads to an increase of unwanted elements such as arsenic, lead, organic matter in the concentrate. Greater amounts of shale complicate copper ore concentration process and cause lower copper recovery at the assumed concentrate grade (Skorupska et al., 2011).

The increasing content of C_{org} , observed in the flotation concentrate throughout the years, is also of significant importance for effectiveness of subsequent pyrometallurgical processes. An increased organic carbon in the final flotation concentrate does not cause much problem for the copper production in the shaft furnace located in Legnica and Glogow, since its presence, due to energy release, is to some degree beneficial, while the C_{org} content exceeding 8% for the one-stage flash furnace disrupts the thermal balance of concentrate melting, effectively decreasing the flash furnace efficiency and increased production cost (Kijewski et al., 2010).

According to KGHM Polska Miedz S.A. strategy, the goal of copper production is a complete replacement of the shaft furnace with the flash smelting technology. Currently, there are two different, shaft furnace and flash smelting technologies, which complement each other, making concentrate management possible. However, due to the target implementation of only flash smelting furnaces in the plant, actions have been taken in order to match the chemical composition of the concentrate for the flash furnace with a focus on appropriate contents of C_{org} , Pb, and S, because the amount of concentrate processed is determined by its calorific value. This requires the furnace feed to have an appropriate composition. It is possible to increase the feed load to the furnace by using cooling aids, but such a technique has limitations. The amount of cooling additives is limited by the process economy, because the cooling additives increase the mass of the slag and generate copper losses in the slag.

Organic carbon removal technologies used throughout the world

Organic carbon removal in the Red Dog mine (Smith et al., 2008)

The Red Dog mine, located in the north part of Alaska near the Arctic Circle, is one of the greatest zinc-lead ore processing plants in North America. The Red Dog ore deposit features, other than its prime chemical elements (Pb, Zn), a great content of organic carbon ($C_{org} = 0.67\%$) which has an adverse effect on its lead and zinc recovery. The problem of organic carbon being present in the Red Dog mine ore was solved by using the so-called “carbon pre-float” process.

The idea behind the process is channeling the material, after grinding and classification in hydrocyclones, to pre-flotation, which results in two products: rich in organic carbon concentrate and poor in carbon waste material, which is the feed for further concentration processes. The pre-flotation process is conducted only in the presence of frother, which makes separation of naturally hydrophobic particles possible. Until 2006 carbon pre-flotation was conducted in flotation machines, however, in order to

increase the effectiveness of organic carbon separation currently Jameson cells are used. The change of the processing system has brought the expected results. The reject of about 70% organic carbon was accomplished.

Organic carbon removal in the Zinifex Century mine (Gredelj et al., 2009)

In the Zinifex Century mine, the main ore mineralization includes galena and sphalerite, while the gangue consists of a large amount of organic matter, which is the main carrier (~3%). The presence of organic carbon is not without consequences in the flotation separation of galena and sphalerite. Due to this, a pre-flotation process has been used in the aforementioned mine for its separation. The effectiveness of the process is conditioned by the application of the *MIBC* (methyl isobutyl carbinol) frother.

Organic carbon removal in the Kittila mine (Doucet et al., 2010)

The Kittila mine is an open-pit and underground gold mine and also a processing-hydrometallurgical complex. Gold is concentrated by flotation due to the fact that it occurs mainly in arsenopyrite in the processed material. The acquired concentrate is leached via a pressure filtering method in POX (Pressure Oxidation) autoclaves, and gold is separated from the solution by using active carbon through the CIL (carbon in leach) technology. There were significant losses of gold following the implementation of this technology caused by its absorption on the organic carbon surface. Its cause was the presence of C_{org} . The technical parameters were improved by separating organic carbon from the feed stream during the pre-flotation stage. In 2009 the separation of 30% C_{org} was accomplished, which translated into gold output increase in the CIL process by 1.5%.

Organic carbon removal in the Mt. Isa mine (Grano et al., 1991)

The Mount Isa mine, located in north-west part of Queensland, is one of the biggest underground copper, zinc and lead mines in the world. Copper and lead-zinc ores are mined and processed separately. The final concentrate produced in Mt. Isa mine's ore concentrator plants during standard flotation would have been heavily contaminated by naturally floating carbonate pyrite, talk and carbon shale. Due to this fact a pre-flotation in the Jameson cell has been applied, in which 2% of the feed mass is separated from the feed stream, of which 50% is actually a naturally hydrophobic material (containing organic carbon), with minimal losses of copper (~0.8%).

Organic carbon removal in KGHM POLSKA MIEDZ SA

The constantly increasing requirements, within the scope of the flash smelting furnace effectiveness in relation to the organic carbon content, were the impulse for undertaking appropriate steps during the processing stage within the framework of the KGHM Polska Miedź S.A. research and development activity. The aforementioned issue has been the subject of a complex research with the goal of developing a method that

would allow for economically and technologically effective production of concentrates featuring stable parameters, in light of present and future metallurgical requirements.

The segregation of the final concentrate into poor and rich in organic carbon via classification in hydrocyclones was performed in Rudna Concentrator Plant in years 2003–2007. This method of classification was causing problems with thickening and filter pressing of the concentrate rich in organic carbon. The product was causing difficulties in the gravity thickening process, resulting in the finest size fraction leaking into the thickeners' overflow, which in turn was causing significant disruptions in the technological process. The results of the conducted research were not satisfactory for the metallurgical industry. That was why the segregation of concentrate into “poor” and “rich” in organic carbon via classification in hydrocyclones was discontinued in 2007.

Due to the lack of possibility to increase the effectiveness of separating the concentrate into products featuring appropriate organic carbon contents and stable quality-quantity parameters in hydrocyclones, especially in the low-carbon concentrate, research has been started in order to develop alternative methods of their production.

Next works utilized differences in flotation kinetics between organic carbon and copper compounds. Due to these features it has been proved, that there is a possibility of segregating the concentrate using the flotation method. This issue became the basis for conducting tests of segregating the concentrate into poor and rich in organic carbon. Positive results allowed to justify the feasibility of conducting a full research cycle, in which research on an industrial scale regarding the diversification of calorific value of the concentrate in flotation process within the framework of a research and development (Trybalski et al., 2010) was conducted. The main goal of their research was to determine the technological possibilities of enhancing the concentrates quality through the reduction of C_{org} content to a level required by the flash smelting technology employed in Glogow Smelter. It has been proved, based upon the results of the research, that by using only the differences in the flotation kinetics of copper sulfides and organic substance a satisfying diversification of two concentrates in terms of the content of these components can be achieved, which satisfy the current needs of the flash furnace and Glogow shaft smelter technology. However, taking into account the continuing modernization of Glogow Smelter, consisting of replacing the shaft technology with the flash smelting technology, additional laboratory and industrial research has been conducted by using chemical reagents. Low-saccharification maltodextrin was used, among others, as an organic carbon depressor (Drzymala, et al., 2011). This test indicated great effectiveness of the reagent in the production of two kinds of concentrate with significant diversification of these components: one rich in Cu and poor in organic carbon and one poor in copper and rich in C_{org} (Foszcz and Drzymala, 2011). Further works in this matter were aimed at the improvement of the final concentrate in Rudna Concentrator Plant (Skorupska et al., 2011). The results of Rudna Concentrator Plant final concentrate flotation tests have confirmed the possi-

bility of producing concentrates featuring diversified chemical compositions, optimal for metallurgical processes (Skorupska et al., 2011).

The results of the mentioned papers, especially the performed economic analysis, has given the authorization to conduct industrial tests of segregating the concentrate with the application of maltodextrine as in the Wroclaw University of Technology patent (Drzymala, et al., 2007). The goal of these tests was to optimize the parameters of the process of increasing segregation in terms of Cu and C_{org} contents in the segregating flotation process and consumption of the reagent and to specify its effect on concentrate dewatering. While it is true that the conducted tests have resulted in having access to the appropriate technology, the broad range of feed variability makes it impossible to produce the concentrate of a stable composition. That is why Rudna Concentrator Plant has taken the different measures in this matter. In order to design the right technology, which would be appropriate from the point of view of processing capabilities and metallurgical requirements, research has begun on developing an optimal concentration variant in order to ensure the production of concentrate featuring reduced C_{org} content, based upon the results and experience of other world producers.

Therefore, the main objective of this paper is to determine the possibility of C_{org} separation during the pre-flotation stage, which may directly cause the reduction of C_{org} content in the scavenger flotation feed and indirectly cause the reduction of C_{org} content in the final concentrate to a level which is acceptable for the flash smelting process.

Experimental

A complex analysis of processing technologies used throughout the world has indicated that KGHM Polska Miedz S.A. is not the only plant struggling with-unwanted occurrence of organic carbon in the ore, and consequently, in the concentrate. The technologies of C_{org} removal outlined already of this paper have become the impulse to undertake appropriate actions in this matter in KGHM Polska Miedz S.A. Division of Concentrators. Several trials and tests were conducted and the results are presented below.

Laboratory flotation

Material from the Polkowice concentrator plant, line II (Fig. 1), was used. The first of the samples was extracted from the \varnothing 500 mm hydrocyclone overflow which is normally fed to the rougher flotation machine MF-222. To this research, the rougher flotation machine was the addition pre-flotation machine (and all required parameters like the collectors and no returned materials from the scavenger and cleaner flotation machines which contain collectors) were met.

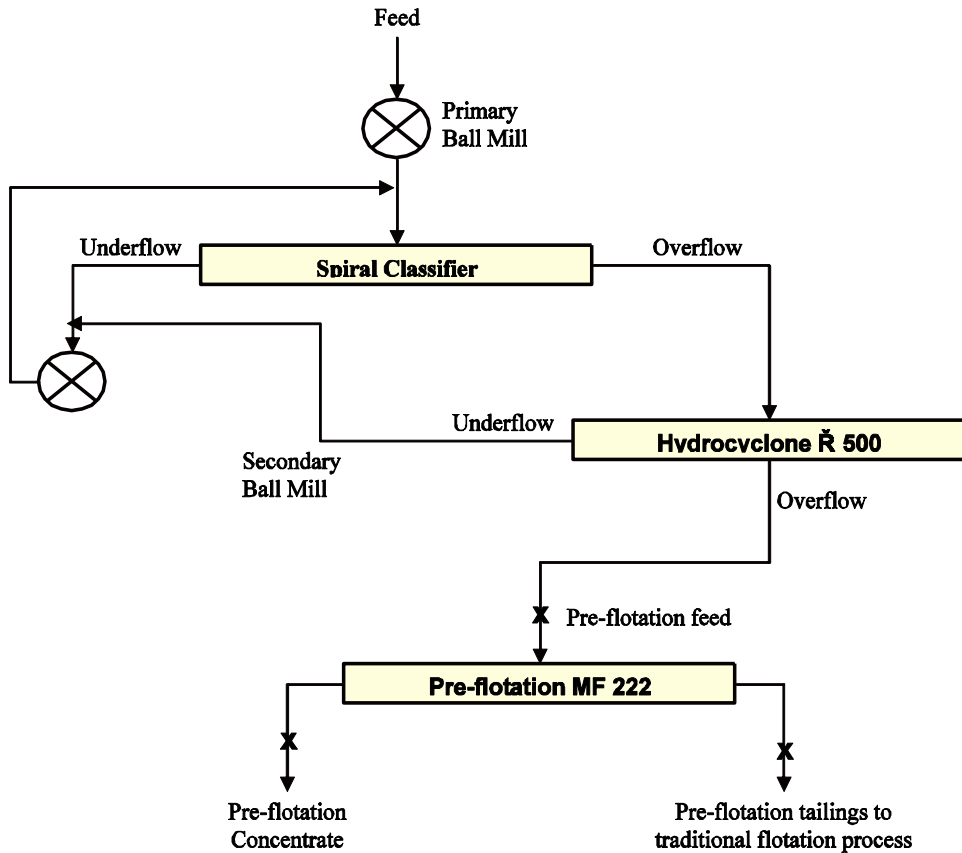


Fig. 1. Schematic block of line II of Polkowice concentrator plant

The scope of the experiments covered two stages: in the first one (experiment I) a comparative laboratory flotation was performed: Flotation A (pre-flotation feed) using Corflot frother (100 g/Mg) and Flotation B (pre-flotation feed) using Corflot frother (60 g/Mg) and collector (a mixture of ethyl and isobutyl sodium xanthate, 120 g/Mg).

The second material used in experiment II was the concentrate from rougher flotation machine MF-222 (obtained only with the application of Corflot frother (100g/Mg, reagent without collectors). The goal of the experiment were to determine the possibility of improved material separation in terms of C_{org} content, and to ensure the possibility of returning as great amount of Cu as possible from pre-flotation concentrate to traditional flotation circuit, thus reducing Cu losses.

The preliminary material extracted from pre-flotation was ground (15 min to 90% >100 μm) and a laboratory flotation was performed by adding only Corflot frother (100 g/Mg).

Both experiments were conducted using a Mechanbor laboratory flotation machine equipped with a 1 dm³ cell. The time of fractional flotation in the experiments was

constant (5 min), while the concentrate was collected after $k_1 = 30$ s, $k_2 = 90$ s, $k_3 = 3$ min, and $k_4 = 5$ min.

The flotation products were dried, weighed and samples were taken for chemical analysis. The determination of Cu and C_{org} content was performed in Quality Control Laboratory, Lubin. Copper was analyzed by using the iodometric titration method, while the organic carbon was analyzed by using a spectrometric method. The results are compiled in Tables 1 and 2 and in Figs 2 to 4.

Research results

The results of conducted laboratory flotation are presented in the form of tables and the Mayer curves in Figs 2, 3 and 4 due to the fact, that the recovery (ε) and the yield (γ) play a significant role in the evaluation of the executed experiments. Because the Mayer curve is sensitive to the feed composition, the location of the upgrading curve depends on the feed. However, a similar content of both Cu and C_{org} in the feed allows a direct comparison of the flotation results of Cu and C_{org} on the same Mayer plot.

A comparison of the results shown in Figs 2 and 3 indicates that the addition of collector has a minimal effect on C_{org} flotation. The reverse situation is observed in case of copper. The addition of collector has a beneficial effect on flotation since it improves flotation selectivity, that is both concentrate recovery and yield. The difference in Cu and C_{org} floatability while using only frother during the pre-flotation stage may, by maintaining proper technological conditions, create a possibility for a satisfying separation of C_{org} from the feed directed for scavenger flotation.

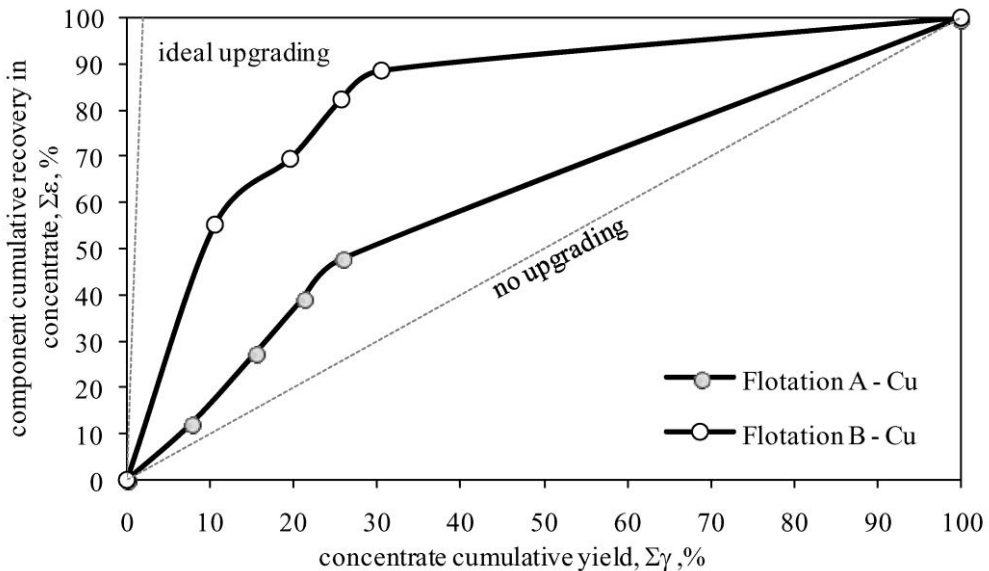


Fig. 2. Results of experiment I – flotation A and B, copper concentration curves

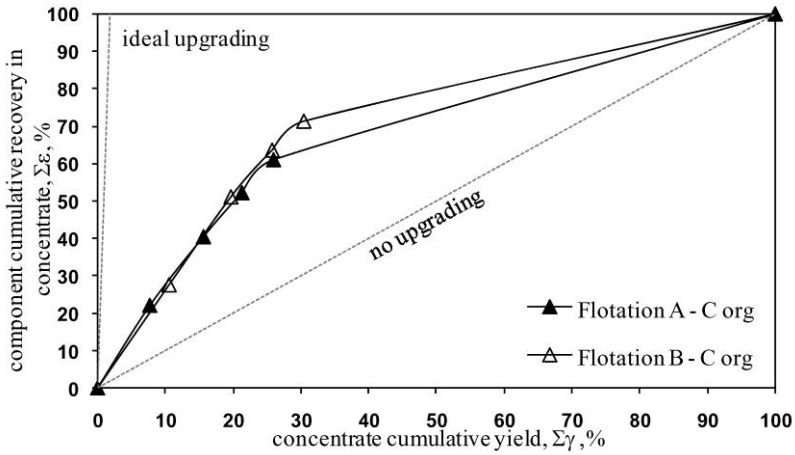


Fig. 3. Results of experiment I – flotation A and B, organic carbon concentration curves

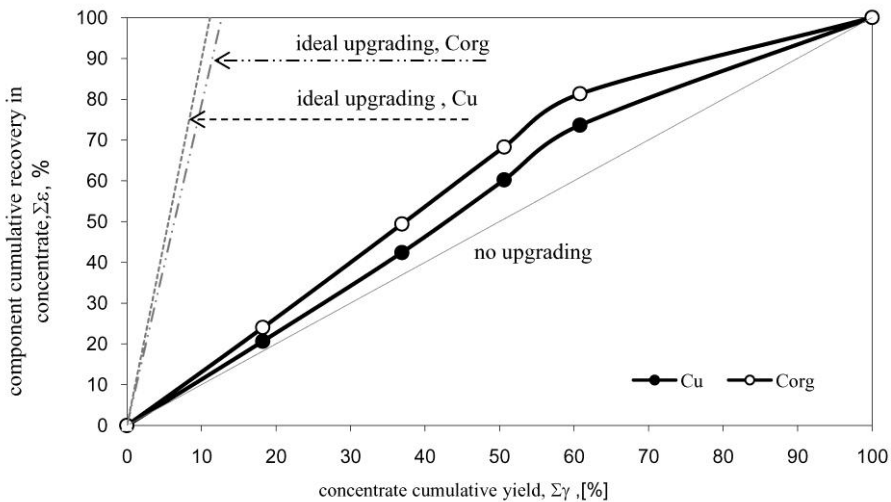


Fig. 4. Results of experiment II – laboratory flotation (Mayer's upgrading curve).
Pre-flotation concentrate with Corflot frother (100 g/Mg)

Figure 4 shows that regrinding and cleaner flotation of the pre-flotation concentrate is justified. Cleaner flotation allows to achieve greater C_{org} content compared to the feed and makes it possible to return about 27% of Cu to the traditional concentration circuit.

The results from experiment I and II confirm the differences in surface characteristics of carbon and copper sulfides, which is directly reflected in their flotation kinetics. Naturally hydrophobic carbon does not require surface modification with a collector,

therefore it floats by using only the frother in the process. Without collector, sulfides exhibit far worse flotation characteristics.

Table 1. Results of experiment I. Flotation A – laboratory flotation without collector. Frother addition (100 g/Mg). λ – content, ε – recovery, γ – yield

Product	Time	γ [%]	$\Sigma\gamma$ [%]	λ_{Cu} [%]	ε_{Cu} [%]	$\Sigma\varepsilon_{Cu}$ [%]	λ_{Corg} [%]	ε_{Corg} [%]	$\Sigma\varepsilon_{Corg}$ [%]
			0			0			0
A/k1	30"	7.72	7.72	3.02	12.21	12.21	4.99	22.01	22.01
A/k2	1'30"	7.81	15.53	3.78	15.46	27.67	4.12	18.38	40.39
A/k3	3'	5.65	21.18	3.94	11.66	39.33	3.68	11.88	52.27
A/k4	5'	4.69	25.87	3.52	8.64	47.97	3.27	8.76	61.03
A/c.		74.13	100.00	1.34	52.03	100.00	0.92	38.97	100.00
Σ		100.00		1.91	100.00		1.75	100.00	

Table 2. Results of experiment I. Flotation B – laboratory flotation with collector (120 g/Mg) and frother (60 g/Mg) addition). λ – content, ε – recovery, γ – yield

Product	Time	γ [%]	$\Sigma\gamma$ [%]	λ_{Cu} [%]	ε_{Cu} [%]	$\Sigma\varepsilon_{Cu}$ [%]	λ_{Corg} [%]	ε_{Corg} [%]	$\Sigma\varepsilon_{Corg}$ [%]
			0			0			0
B/k1	30"	10.58	10.58	8.36	55.31	55.31	4.27	27.69	27.69
B/k2	1'30"	9.02	19.60	2.53	14.28	69.59	4.26	23.57	51.26
B/k3	3'	6.12	25.72	3.35	12.82	82.41	3.29	12.34	63.59
B/k4	5'	4.78	30.50	2.10	6.28	88.69	2.68	7.86	71.45
B/c.		69.50	100.00	0.26	11.31	100.00	0.67	28.55	100.00
Σ		100.00		1.60	100.00		1.63	100.00	

Table 3. Results of experiment II. Laboratory flotation of concentrate from pre-flotation machines MF-222 (with Corflot 100 g/Mg). λ – content, ε – recovery, γ – yield

Product	Time	γ [%]	$\Sigma\gamma$ [%]	λ_{Cu} [%]	ε_{Cu} [%]	$\Sigma\varepsilon_{Cu}$ [%]	λ_{Corg} [%]	ε_{Corg} [%]	$\Sigma\varepsilon_{Corg}$ [%]
			0			0			0
II/k1	30"	18.23	18.23	12.63	20.64	20.63	16.76	24.01	24.01
II/k2	1' 30"	18.67	36.90	13.02	21.78	42.40	17.31	25.38	49.39
II/k3	3'	13.72	50.62	14.48	17.81	60.20	17.52	18.89	68.27
IIk4	5'	10.17	60.80	14.74	13.44	73.63	16.31	13.03	81.31
II/c.		39.20	100.00	7.51	26.38	100.00	6.07	18.69	100.00
Σ		100.00		11.16	100.00		12.73	100.00	

Industrial trials

The positive results of the experiments conducted on a laboratory scale have decided in favor of conducting the test on a technical scale. In order to determine the validity of the assumed thesis that there is a possibility of organic carbon separation during pre-flotation stage under KGHM Polska Miedz SA Division of Concentrators industrial conditions comparative tests of pre-flotation stage process effectiveness were conducted (Polkowice Concentrator Plant, line II, Fig.1).

The basis of the test is the comparison of the processes run under industrial conditions. The tests were conducted on three-cell flotation machine with an overall capacity of 144 m³ under comparable conditions. Analogous settings of froth level and air flows were used for both test stages, which were respectively 15 cm and 6 m³/min.

The effectiveness of the process while adding the reagents in normal way and while performing current production was analyzed in the first test – (Corflot, ~40 g/Mg) and collector (a mixture of ethyl and isobutyl sodium xanthate, ~60 g/Mg). The second stage of the experiment took place only in the presence of a frother (Corflot, ~80g/Mg).

Trial results

The analysis of product produced while conducting the experiments (feed α , concentrate β , tailings ν) is presented in from Figs 5 to 7.

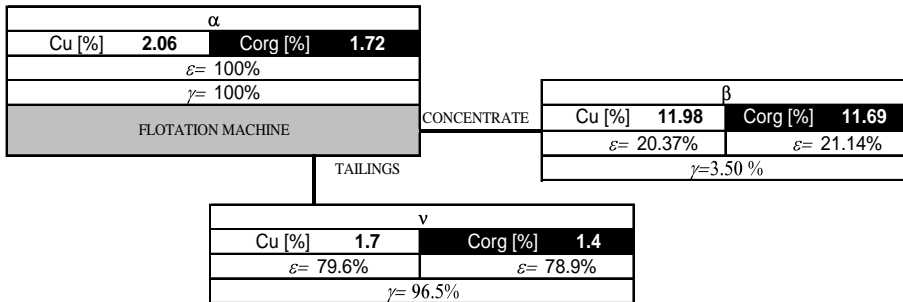


Fig. 5. Trial 1. Results of flotation machine sampling–test included collector and Corflot frother, ~40 g/Mg, xanthate, ~60 g/Mg

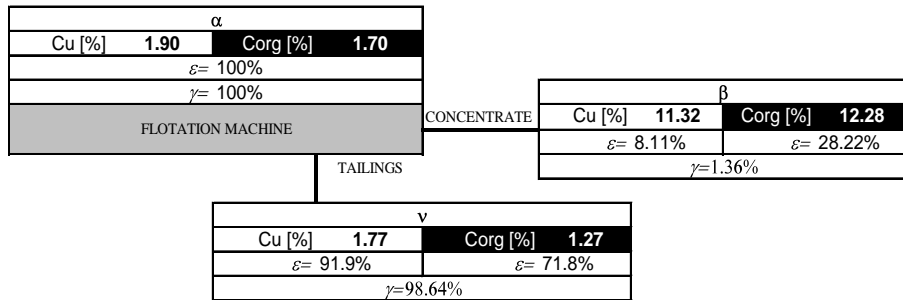


Fig. 6. Trial 2. Results of flotation machine sampling–test. Corflot frother only, ~80g/Mg

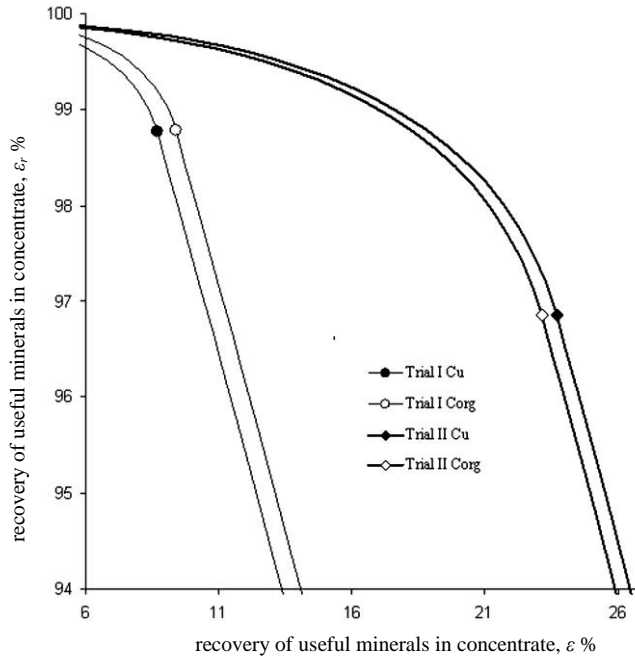


Fig. 7. The Fuerstenau curve for industrial trial of pre-flotation of Cu and C_{org}

Based upon the approximate results of the trials (Figs 5 and 6) also presented in Fig. 7, a comparison of C_{org} and Cu concentration performance under industrial conditions indicates noticeable differences in recovery and yields of the concentration process products (concentrate, tailings) in relation to the conditions of the conducted experiment i.e. the application of a collector reagent and its absence during the process.

Results and discussion

The analysis of the obtained results shows, that there is a possibility of separating significant amounts of organic carbon on the pre-flotation stage by applying only the frother. In comparison to flotation with collector, flotation in which a frother was used about 28% of organic carbon contained within the feed was successfully separated, thus reducing its content from 1.7 to 1.27% with minimal copper losses of 8.1%. The insubstantial yield of the concentrate and the organic carbon content of 12.26% has a beneficial effect on this process, which results from the further processing of the produced concentrate i.e. regrinding and purification in order to return as great amount of copper back to the process as it is possible.

The results of the conducted research allow for the following conclusion:

- flotation kinetics of the organic matter without application of collector is much better than the flotation kinetics of copper sulfides

- separation of organic carbon during the pre-flotation stage under KGHM Polska Miedz S.A. Division of Concentrators conditions is possible
- produced concentrate, featuring greater content of organic substance, can be made a subject to regrinding and cleaning flotation in order to return significant amounts of copper to the conventional concentration process
- Corflot frother used during the tests was applied in order to ensure the appropriate run of the process. Other frother, used for instance in coal flotation, will be tested.

Division of Concentrators is where solutions to the most important problems occurring in concentration technologies are being sought within the framework of research and development activity. However, the problem of organic carbon extends beyond the framework of processing technologies due to the fact, that it is a global problem, because it has an influence on the economic-technological effectiveness of the entire company. That is why this subject is researched in such a complex way and analyzed by the concentrator staff. In order to meet the expectations of present and future metallurgical requirements many possibilities of adapting the concentrate quality to metallurgical requirements were researched and tested, some of which are not possible to implement in current production. That is why the described here actions, which were initiated by the employees may be the turning point in the production of concentrate featuring appropriate quality both for the target technology in the form of flash smelting furnace technology. however, it requires further research due to the fact, that the results presented within this paper are of diagnostic nature.

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