

# The behavior of oxidized copper during the sulphide Cu ore flotation in KGHM Polska Miedź S.A.

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**Abstract.** The work included a synthetic review of the occurrence of oxidized Cu minerals in the concentrators belonging to KGHM Polska Miedź S.A. and problems occurring in the flotation of oxidized Cu ores. The course of flotation of oxidized copper in concentrators A, B and C was examined on the basis of archival results and specialized sampling campaigns. It was found that the content of oxidized copper in the flotation tailings ranges from 0.015-0.05%, and in the concentrate from 0.23 to 0.72%. The share of oxidized copper is highest in the case of flotation tailings and ranges from 10.7 to 25.7%.  $\text{Cu}_{\text{ox}}$ 's share is only a few percent in concentrates. Analyzing the average annual balance samples, the  $\text{Cu}_{\text{ox}}$  contents were clearly higher for all concentrators than for the sampling campaign samples, which, as indicated, is caused by the long storage time of the analytical samples. Evaluations of revenues from  $\text{Cu}_{\text{ox}}$  recovery were made and a further directions of research on the recovery of oxidized copper from flotation tailings were proposed.

## 1. Introduction

Flotation, and then smelting the concentrate obtained in this way, has been the most popular method of producing basic metals for more than 100 years, in particular Cu. The standard in the copper industry is currently the quality of flotation concentrates at the level of approx. 25% Cu, with a recovery at the level of 90%. Such a high level of indexes can be achieved, however, only when the predominant form of occurrence of copper are sulphides. In practice, copper sulphides are often accompanied by oxidized copper minerals, and sometimes they can be the only form of Cu occurrence. The results of flotation of ores with an elevated content of oxidized Cu minerals, even after applying special flotation conditions, are usually worse, or much worse, than sulphide ores and are frequently characterized by high variability.

The primary reason for the presence of oxidized copper minerals is the genesis of the deposit, but in certain circumstances, secondary oxidation of mineral surfaces may occur, especially in the finest classes, which generally causes deterioration of concentration indexes. The reasons for the secondary oxidation of sulphide Cu minerals are most often: long-term storage of ore, too fine grinding and/or long flotation times.

The method of processing of oxidized Cu deposits depends each time on the type and manner of occurrence of oxide forms, gangue composition, variability of oxidized minerals, content levels of individual Cu forms, etc. In the case of clearly defined, oxidized parts of the deposit, the most appropriate method of their processing is usually the selective exploitation and separate processing of both types of ores by methods adapted to their properties: e.g. by separate flotation of sulphides and oxides or hydrometallurgy. Depending on specific conditions, other solutions are also possible.



The matter of flotation of oxidized Cu minerals contained in the deposits of KGHM Polska Miedź S.A., due to their minimal content and expected, quite limited economic effects is a difficult issue and requires the inclusion of a number of restrictions. For these reasons, it has so far been recognized only fragmentarily, while conducting other research.

This paper presents the results of research on the occurrence of total and oxidized copper in the balance products of all concentrators belonging to KGHM Polska Miedź S.A., the analysis of its behavior in the process of industrial flotation and the estimation of feasibility  $\text{Cu}_{\text{ox}}$  recovery improvement.

## 2. Occurrence of oxidized Cu minerals in copper ores converted in KGHM

More than 120 oxidized copper minerals are known, but as practice indicates, commercial meaning is primarily malachite and azurite, to a lesser extent cuprite, tenorite and chrysocolla. The most important properties of selected oxide copper minerals are given in table 1.

**Table 1.** The most important properties of selected copper oxide minerals found in the KGHM Polska Miedź S.A. [1].

Mineral	Chemical formula	Cu content, (%)	Mosh hardness	Specific weight, ( $\text{Mg/m}^3$ )	Color
Cuprite	$\text{Cu}_2\text{O}$	88.8	3.5-4.0	5.9	Brick-red
Tenorite	$\text{CuO}$	80.0	3.5	6.5	Black
Azurite	$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$	55.3	3.5-4.0	3.7	Blue
Malachite	$\text{Cu}_2(\text{OH})\text{CO}_3$	57.4	3.5-4.0	3.9	Green
Chrysocolla	$(\text{Cu};\text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$	10-36	2.0-4.0	2-2.4	Blue

In the geological documentation of the copper deposit KGHM Polska Miedź S.A., made in 1958-1960 by the Geological Enterprise and the Polish Geological Institute from Warsaw, only cuprite and tenorite were identified from the oxidized copper minerals. It was only in later years that azurite, malachite and chrysocolla were discovered [2]. Due to the minimal content of individual Cu oxide minerals and the variability of oxide mineralization, the identification of oxide forms - even using the latest mineralogical techniques (e.g. MLA) - is difficult and usually requires confirmation by other methods.

Researching the influence of dry grinding on the results of Cu copper ore flotation, identification of the mineral composition and the degree of release of Cu minerals in the feed for Polkowice concentrator were carried out using the MLA method. Of the oxidized Cu minerals, only cuprite (0.01% by weight) was identified [3].

In mineralogical studies of a larger number of tailing and concentrate samples from laboratory flotation of Rudna ore, the presence of cuprite at the level of 0.06% by weight - concentrate, and in tailings of 0.001 - 0.0001% by weight, was shown [4]. The presence of atacamite was also found: in tailings at 0.005-0.010% by weight, and in the concentrates of 0.035-0.017% by weight. So far, none of the mines of KGHM Polska Miedź S.A. it was not possible to discover the oxidized parts of deposit that could be subject to exploitation or even the place for sampling for laboratory tests. This indirectly indicates the low level of oxidation of the deposit and the possibility of occurrence of only minimal content of oxidized Cu minerals, both in the feed and in the concentration products. The phenomenon of oxidation of sulphide Cu minerals is well known both in the mines of KGHM Polska Miedź S.A. - as so-called "green walls" as well as on rework - as so-called "weathered ore". Flotation results of the ore exposed to air are the worse the longer the ore storage time [5]. However, the

studies carried out have shown that this process is quite slow and in the initial phase minimally affects the results of flotation. Such dependencies were found for both Lubin and Polkowice ores [6, 3]. In addition, it should be noted that the degree of deterioration of the flotation results depends to a large extent on the adopted research methodology and/or flotation technology.

### 3. Global practice of processing oxidized copper ores

Poor floatability of oxidized copper ores has been widely known for a number of years (e.g. [6-10]. Generally, for the processing of oxide copper ores, two methods are used: 1) hydrometallurgical, and; 2) flotation, but for a long time the hydrometallurgical method (SX-EW) has dominated the technique of processing oxidized and mixed copper ores [11-13]. The hydrometallurgical method is by far the most appropriate in the form of heap or dump leaching [11]. In the case of mixed ores, leaching is usually supported by the activity of microorganisms [13, 14]. The floatability of individual Cu oxide minerals is very diverse [7-10, 15, 16]. Of the oxidized copper minerals, chrysocolla ( $\text{Cu; Al} \text{ }_2\text{H}_2\text{Si}_2\text{O}_5 \text{ (OH)}_4 \cdot n\text{H}_2\text{O}$ ), was the most common object of flotation research, but for Cu production the most important mineral from this group is malachite ( $\text{Cu}_2\text{(OH)CO}_3$ ). Its relatively good - against other oxide minerals Cu - floatability has been confirmed by many studies. Azurite ( $\text{Cu}_3\text{(OH)}_2 \text{ (CO}_3)_2$ ) also floats quite well, similar to malachite, which is reflected in the data from a number of enrichment plants. The Kuprite ( $\text{Cu}_2\text{O}$ ) requires higher doses of the sulphidising agent than other minerals, and the flotation behavior of the tenorite ( $\text{CuO}$ ) is close to cuprite. As for other Cu oxidized minerals, such as atacamite ( $\text{Cu}_2\text{Cl(OH)}_3$ ), or brochantite ( $\text{Cu}_4\text{(OH)}_6\text{SO}_4$ ), their floatability was not investigated.

Although there are many examples of good results of oxidized Cu flotation in the laboratory scale, the practice is quite poor, due to a number of difficulties occurring in industrial conditions. The most important of them include natural variability of the deposit and brittleness of oxide minerals. Due to the brittleness of many oxide minerals, copper tends to crumble in the process of processing and going to the fine classes, which further complicates their flotation. The individual flotation reagents have their own specific limitations, which can also contribute to the deterioration of the flotation results.

Generally, three basic methods of flotation of oxidized Cu ores are used:

1. Flotation after previous sulphidisation of the surface of Cu oxide minerals.
2. Direct flotation of Cu oxidized minerals using fatty acids and their soaps
3. Direct flotation using a new type of reagents.

The most popular method of flotation of Cu oxide minerals is the prior sulphidisation of oxide mineral surfaces using different types of sulphides ( $\text{NaHS}$ ,  $\text{Na}_2\text{S}$  and  $\text{(NH}_4)_2\text{S}$ ), followed by flotation using thiol collectors. This method has been used in a relatively large number of concentrators, e.g. in China, Africa and other countries [17-20].

The practical implementation of flotation with sulphidisation is difficult because too little addition of the sulphidising reagent will cause only some oxide particles to be flotated, and too much - their depression [21, 22]. In both cases the flotation results will be worse than they could be. In laboratory conditions, the controlled redox method (CPS - Controlled Potential Sulphidisation) is very helpful, but it fails in industrial conditions. In addition, the optimal dose of the sulphidising reagent depends primarily on the mineral composition of the ore to be treated, on the time and manner of the ore conditioning, the method of mixing and other variables [8]. These are factors that are largely out of control in industrial conditions, which results in an unacceptably high fluctuation in the oxide ore flotation results. In the largest part, this is due to the natural variability of the deposit, which seriously hinders, or even practically prevents, applying the appropriate dose of the sulphidising agent.

For flotation of sulphidized Cu oxide minerals, the most commonly used are xanthates or other reagents designed for sulphide flotation - usually with a longer hydrophobic chain. In relation to sulphide ores, flotation of oxidized ores is characterized by reduced selectivity and reduced yields. For example, in the Cu-Co ore processing plant using  $\text{NaHS}$ , in Katanga, Democratic Republic of the Congo, about 77% Cu and 75% cobalt were recovered, with a concentration ratio of just 3.0 [23]. If the  $\text{NaHS}$  and  $\text{(NH}_4)_2\text{S}$  mixture was used as the sulphidising agent in the ratio 1:1, the concentration results were slightly better: the recovery was about 80% for Cu and Co, and the enrichment ratio was 3.5.

The second, less popular method of flotation of oxidized Cu ores, without the need for prior sulphidisation, is the use of fatty acids and their soaps. Such reagents are best suited for quartz or silicate gangue, because they cannot be used if gangue contains  $\text{Ca}^{+2}$  ions in its composition, e.g. limestone, dolomites, etc.

Due to specific flotation disadvantages when both sulphidisation and fatty acids are used, long-lasting attempts to find other reagents for direct flotation of oxide copper minerals have been sustained. On the laboratory scale, satisfactory results were achieved with a number of reagents, such as complexing reagents, fatty amines, petroleum sulphates, but in an industrial scale, the number of applications of these new compounds was very limited [24]. In this group, one of the most interesting reagents is hydroxamic acid and its various alkyl hydroxamates (R-CHONHO) [20]. Its biggest advantage of hydroxamates is their higher selectivity than the reagents currently used for flotation of oxidized ores [23].

These difficulties in controlling the flotation process, fairly low concentration ratios, high costs of using special flotation reagents and the established position of hydrometallurgical methods mean that currently relatively few Cu oxide ores are processed using the flotation method [21].

#### 4. Identification and analysis of the behavior of oxidized copper in the industrial enrichment process

##### 4.1. Oxidized copper behavior in the flotation process - balance results

Work on identifying the behavior of oxidized copper in flotation circuits began with the collection and analysis of annual technological results for all concentrators of KGHM Polska Miedź S.A. Table 2 gives the average results of the content of oxidized copper in balance products i.e. Feed (F), Tailings (T) and Concentrate (C) for the years 2000-2015 and the calculated on this basis the average concentration ratios (CR) and recoveries (R). The same table also gives the fundamental statistics calculated for these results, such as minimum and maximum value, standard deviation (SD) and relative standard deviation (RSD).

**Table 2.** Average annual  $\text{Cu}_{\text{ox}}$  content in the balance products of concentrators, the most important concentration indexes and selected statistics for the concentrators A, B and C in the years 2000-2015.

Statistics	Concentrator A					Concentrator B					Concentrator C				
	F, %	T, %	C, %	CR	R, %	F, %	T, %	C, %	CR	R, %	F, %	T, %	C, %	CR	R, %
Average	0.15	0.5	0.79	5.6	68.1	0.23	0.09	1.07	4.7	64.0	0.29	0.09	1.21	4.23	73.7
Population	16	16	16	16	16	11	11	11	11	11	6	6	6	6	6
Max	0.22	0.08	0.98	7.7	76.8	0.26	0.10	1.23	5.3	72.9	0.30	0.10	1.44	4.86	76.43
Min	0.09	0.04	0.58	3.7	48.7	0.20	0.08	0.85	3.3	55.3	0.25	0.08	1.07	3.57	71.47
SD	0.04	0.01	0.12	1.3	7.59	0.03	0.01	0.11	0.65	8.05	0.02	0.01	0.13	0.48	1.73
RSD	24.4	20.2	14.6	23.4	11.1	12.2	8.2	10.0	13.7	12.6	6.0	7.5	10.5	11.4	2.30

The content of oxidized copper in tailings from the concentrator B and C amounts to 0.23 and 0.29% respectively, while the smallest content is observed for plant A, where it is 0.15%. The relatively highest - though still small - oxidized copper content is observed in concentrates: in the case of concentrate from plant C,  $\text{Cu}_{\text{ox}}$  content reaches on average to 1.21%, and in the case of B concentrate it is slightly lower and amounts to 1.07%. The fact of occurrence of  $\text{Cu}_{\text{ox}}$ 's largest contents in concentrate, and the smallest - in wastes is quite surprising.

The very good recoveries of oxidized copper, exceeding 60%, are also surprising, with the case of plant C equal to 73.7%.

Due to the mechanism of behavior of oxidized copper in the flotation process one would expect both lower  $\text{Cu}_{\text{ox}}$  contents in concentrates and significantly lower recoveries. However, the results are opposite. The explanation may be - at least in part - secondary oxidation of sulphides, as a result of long-term storage of analytical samples under conditions of air access.

The variability of the content of oxidized copper in all concentration products and in all concentrators was also analyzed, as well as variability of recovery and concentration ratio. Comparing these parameters with the analogous  $\text{Cu}_{\text{tot}}$  variations determined in the research carried out in previous years, the variability of results for oxidized copper turns out to be generally slightly higher than for total copper. It should be emphasized that comparing  $\text{Cu}_{\text{ox}}$  and  $\text{Cu}_{\text{tot}}$ , the least variability of such indexes as recovery and copper content in concentrate is usually obtained by  $\text{Cu}_{\text{tot}}$ . This is the result of the company's conscious policy of stabilizing the most important concentration indexes.

In order to determine the possible relationships between particular parameters, correlation coefficients were calculated for the relationship between the content of  $\text{Cu}_{\text{tot}}$ ,  $\text{Cu}_{\text{ox}}$ , oxidation degree and recovery. In the vast majority of cases, the value of correlation coefficients turned out to be low or very low. The very low values of correlation coefficients between the  $\text{Cu}_{\text{ox}}$  content in the feed and the Cu recovery for all concentrators turned out to be particularly surprising. However, this is not a proof of the lack of significant dependencies between the analyzed variables, it only means that these relationships have not been revealed in the specific conditions of the analyzed population of results. The most important conditions include quite low level of oxidized Cu - in particular in flotation tailings and feed, behavior of  $\text{Cu}_{\text{ox}}$  in the flotation process and - first of all - accuracy of chemical analyzes and observed range of variability of analyzed parameters, especially  $\text{Cu}_{\text{ox}}$  content.

#### *4.2. Behavior of oxidized copper in the flotation process – the results of sampling*

In this subsection, the same abbreviations for balance products and concentration indexes as in subsection 4.1 were used.

*4.2.1. Collection and analysis of concentration products.* Due to the long-term storage of balance samples under conditions of free air access, it is possible that the results of the determination of the oxidized copper content are overstated. Therefore, a decision was made to carry out specialist sampling. Sampling balance products, i.e. feed, tailings and concentrate, in all concentrators of KGHM Polska Miedź S.A. was carried out from August 16 to 19, 2016, for a period of 9 shifts. The samples were then dried, averaged, reduced, ground and thoroughly mixed. The content of total Cu and CuO was determined in the prepared samples. The sampling and determination of the content of the listed components were carried out by the Center for Quality Research in Lubin

*4.2.2. Results and their discussion.* Using the obtained results of analyzes of industrial concentration products,  $\text{Cu}_{\text{ox}}$  content and its shares in particular concentration products in relation to  $\text{Cu}_{\text{tot}}$  were calculated as well as basic concentration indexes such as concentrate yield, CR (Concentration Ratio) and R (Recovery) for both total Cu, and oxidized. Obtained results of testing and results of calculations are given in table 3.

The  $\text{Cu}_{\text{ox}}$  contents found in all cases in samples taken during specialist sampling are clearly lower than for average annual samples. In turn,  $\text{Cu}_{\text{ox}}$  recoveries are smaller. This confirms the thesis about the oxidation process as a result of long-term stored analytical samples. What is surprising is the fact of  $\text{Cu}_{\text{ox}}$ 's high recoveries, as the technological flow-sheets of KGHM Polska Miedź SA's concentrators as well as the reagent regime in force are only suited to the recovery of sulphides. In the concentrator B, more than half of the oxidized copper contained in the feed is recovered, and in plant C almost 70%. Similar results, taking into account differences in the quality of the concentrates, were obtained during laboratory flotation experiments with the ore from plant C: after 30 minutes of reference flotation, using the same flotation reagents as in the industry,  $\text{Cu}_{\text{ox}}$  recovery was 80.7% with a  $\text{Cu}_{\text{tot}}$  yield of 91.7%.

**Table 3.** Average Cu, CuO and Cu<sub>ox</sub> contents in the balance products of A, B and C concentrators and basic concentration indexes for Cu<sub>ox</sub> and Cu<sub>tot</sub> – sampling campaign.

Specification	Content, %			Yield, %	CR	R, %
	F	T	C			
<b>Concentrator A</b>						
Cu, %	0.98	0.14	14.58	5.82	14.9	86.5
CuO, %	0.046	0.019	0.288	10.04	6.3	62.8
Cu <sub>ox</sub> , %	0.0368	0.015	0.230	10.04	6.3	62.8
Share of Cu <sub>ox</sub> , %	3.76	10.86	1.58	-	-	-
<b>Concentrator B</b>						
Cu, %	1.68	0.21	25.57	5.80	15.2	88.2
CuO, %	0.13	0.068	0.825	8.19	6.3	52.0
Cu <sub>ox</sub> , %	0.104	0.054	0.66	8.19	6.3	52.0
Share of Cu <sub>ox</sub> , %	6.19	25.90	2.58	-	-	-
<b>Concentrator C</b>						
Cu, %	1.66	0.20	26.49	5.55	16.0	88.6
CuO, %	0.098	0.034	0.895	7.43	9.1	67.9
Cu <sub>ox</sub> , %	0.078	0.027	0.716	7.43	9.1	67.9
Share of Cu <sub>ox</sub> , %	4.72	13.60	2.70	-	-	-

**Table 4.** The results of sieve analysis and contents of Cu<sub>tot</sub>, CuO and Cu<sub>ox</sub> in the individual particle classes of flotation tailings in concentrators A, B and C –sampling campaign.

Particle size +, mm	Yield, w/w%	Cum. yield passing, w/w%	Content			Share of Cu <sub>ox</sub> , %	Distribution, %		
			Cu, %	CuO, %	Cu <sub>ox</sub> , %		Cu,	CuO	Cu <sub>ox</sub>
<b>Concentrator A</b>									
0.125	16.7	83.3	0.22	0.015	0.012	5.5	29.3	13.0	13.0
0.100	35.7	47.6	0.07	0.008	0.006	9.1	19.9	14.8	14.8
0.075	10.2	37.4	0.08	0.012	0.010	12.0	6.5	6.3	6.3
0.036	11.0	26.4	0.12	0.017	0.014	11.3	10.5	9.7	9.7
-0.036	26.4	-	0.16	0.041	0.033	20.5	33.7	56.1	56.1
F	100.0	100.0	0,13	0,019	0,015	12,3	100,0	100,0	100,0
<b>Concentrator B</b>									
0.125	13.7	86.3	0.15	0.020	0.016	7.3	8.7	4.6	4.6
0.100	17.2	69.1	0.27	0.032	0.026	9.5	19.7	9.2	9.2
0.075	9.7	59.4	0.32	0.043	0.034	10.8	13.2	7.0	7.0
0.036	15.3	44.1	0.32	0.040	0.032	10.0	20.8	10.3	10.3
-0.036	44.1	-	0.20	0.093	0.074	37.2	37.5	68.9	68.9
F	100.0	100.0	0.24	0.060	0.048	20.3	100.0	100.0	100.0
<b>Concentrator C</b>									
0.125	31.3	68.7	0.22	0.015	0.012	5.5	32.8	14.8	14.8
0.100	37.1	31.6	0.13	0.017	0.014	10.5	23.0	19.8	19.8
0.075	9.5	22.1	0.25	0.026	0.021	8.3	11.3	7.8	7.8
0.036	8.5	13.6	0.30	0.038	0.030	10.1	12.2	10.2	10.2
-0.036	13.6	-	0.32	0.111	0.089	27.8	20.7	47.5	47.5
F	100.0	100.0	0.21	0.025	0.032	15.2	100.0	100.0	100.0

Most strikingly, the  $\text{Cu}_{\text{ox}}$  concentration ratios given in table 3 for all concentrators are high, amounting to 6.3 (concentrator A and B), and even very high - 9.1 (plant C).

All these results show clearly better concentration of Cu oxide minerals found in Polish copper ores than in other ores described in the literature [23].

To assess the possibility of Cu recovery from flotation tailings, one of the most important issues is: the form of copper occurrence and its distribution in individual particle classes. Table 4 presents the results of sieve analysis and the content and distribution of selected components (Cu,  $\text{CuO}$   $\text{Cu}_{\text{ox}}$ ) in individual particle classes of flotation tailings from all concentrators.

Depending on the plant, the largest contents of  $\text{Cu}_{\text{tot}}$  in flotation tailings are observed in different classes: in the case of concentrator A it is the thickest class, in the case of plant B - these are intermediate classes, and in the case of plant C - it is the smallest class. The distribution of total copper in individual particle classes generally shows a fairly good correlation with the yield of a given class.

In the case of  $\text{Cu}_{\text{ox}}$ , its largest content, for all plants, is observed in the smallest class of flotation tailings - below 36  $\mu\text{m}$ . The  $\text{Cu}_{\text{ox}}$  distribution is also similar: for all concentrators, oxidized copper accumulates mainly in the class below 36  $\mu\text{m}$ . For concentrators A and B, in the smallest class, it collects more than twice as much  $\text{Cu}_{\text{ox}}$  than the outgoings of this class, and in the case of plant C - more than three times more. As a result, almost  $\frac{3}{4}$  of oxidized copper accumulates in the smallest particle class - in the case of plant B, and more than half or nearly half of this form of copper - in plants C and A, although the share of the smallest class of flotation tailings in these plants is only 26.4 (A), 44.1 (B) and 13.6% (C).

The highest content of oxidized copper is observed in final concentrates (see table 3). They range from 0.23% Cu - for plant A, through 0.66% - for plant B, to 0.72% - for plant C. However, due to the high copper content of the concentrates, the  $\text{Cu}_{\text{ox}}$  shares in the concentrates are clearly smaller than in tailings or in the feed, which is consistent with the oxide flotation model.

## 5. Perspectives for the recovery of oxidized copper from flotation tailings

The observed, very low content of oxidized copper in flotation tailings determines the maximum possible level of income from recovery of oxidized copper and the type of concentration methods and equipment that could be used for this purpose.

Table 5 shows the value of recoverable oxidized and total copper from flotation tailings of individual concentrators.

**Table 5.** The value of recoverable oxidized and total copper included in flotation tailings of concentrators A, B, and C.

Concentrator	Ore throughput dry mass		Tailing yield, (%)	Cu content in tailings, (%)		Recoverable copper mass in tailings, (Mg)		Value of recoverable Cu, (mln USD)	
	(Mg/d)	(Thous. Mg/rok)		$\text{Cu}_{\text{ox}}$	$\text{Cu}_{\text{tot}}$	$\text{Cu}_{\text{ox}}$	$\text{Cu}_{\text{tot}}$	$\text{Cu}_{\text{ox}}$	$\text{Cu}_{\text{tot}}$
A	22 450	8 194	94,21	0,015	0,13	1 229	10 653	7,3	62,8
B	25 180	9 191	94,06	0,054	0,20	4 963	18 381	29,3	108,5
C	45 580	16 637	93,99	0,027	0,18	4 492	29 946	26,5	176,7
Total	93 210	34 022	-	-	-	10 684	58 980	63,0	348,0

The calculations involved ore throughputs and contents of  $\text{Cu}_{\text{tot}}$  and  $\text{Cu}_{\text{ox}}$  in flotation tailings actually produced in individual concentrators. The copper price was adopted at USD 5.900 per Mg. In the absence of appropriate studies, it was assumed optimistically that the recovery of oxidized Cu from flotation tailings will amount to 60%.

The estimation of the value of oxidized copper, which can theoretically be recovered from flotation tailings, is quite attractive at first sight, especially in the case of plants B and C, but the remaining aspects

of the possible recovery process should be considered, especially the assumed level of capital and operating costs.

To further specify the above estimates, it is necessary first and foremost to perform laboratory tests to determine the actual indicators for the concentration of oxidized copper. Based on the literature information [9, 14-17, 19-20, 24], it can be predicted that the Cu contents in the flotation concentrate will be of the order of at most a few percent, if a satisfactory recovery is to be achieved. This is too low a value for this type of product to be considered as a qualified concentrate. After applying an appropriate sales formula to such a concentrate, the value of recovered copper will significantly decrease in relation to the values given in table 6, even if the recovery is maintained at 60%.

Another unfavorable factor is the low content of  $\text{Cu}_{\text{ox}}$  in flotation tailings in all concentrators as well as properties of the slurry of produced flotation tailings. It can be anticipated, the required number of flotation cells will be significant, which will translate into high capital and operating costs. One should also expect additional, significant investment outlays to increase the milling power. With interesting but not very high incomes (see table 5), it is essential to invest very economically, for example by shortening the flotation time of oxides through e.g. the intensification and/or implementation of oxide flotation in the final phase of the main sulphide flotation or by other ways. Confirmation of such possibilities also requires conducting appropriate tests.

Due to the low  $\text{Cu}_{\text{ox}}$  content in the flotation tailings, the technology that guarantees the simultaneous recovery of sulphide and oxide copper would be much more rational. This would significantly increase the level of income. Table 5 shows the mass of recoverable total (sulphide and oxide) copper found in the tailings and its value, assuming the same recovery for both type of copper as before. In this case, the revenues are about 6 times higher than in the recovery of only oxidized copper. It means that the margin for investment is clearly larger. Even higher revenues could be obtained by using hydrometallurgical methods, which would allow the recovery of both sulphide and oxidized copper, with higher recoveries than in the case of flotation only.

It seems, therefore, that further research should be carried out in this direction, despite the fact that previous experience with the recovery of copper from tailings by flotation, hydrometallurgical method or hybrid method indicates that even for such a technology obtaining the profitability of an investment will be difficult [10].

## 6. Summary and conclusions

1. Based on the previous diagnosis, oxidized copper contained in the feed processed at individual concentrators of KGHM Polska Miedź S.A. occurs primarily as cuprite, tenorite, azurite, malachite and chrysocolla. The presence of other  $\text{Cu}_{\text{ox}}$  minerals is so far doubtful.
2. The share of oxidized copper - determined on the basis of long-term average annual results - in the feed of all concentrators is slightly more than 10% of total copper, in tailings - from 27.1% to 38.6%, and in concentrates not more than 4.1%. Shares of oxidized copper in samples of feed, tailings and concentrate collected during sampling on August 16-19, 2016, are clearly smaller than the data cited above, which is understandable due to the chemistry of the oxidation processes.
3. On the basis of specialist sampling, it was found that the content of oxidized copper in the flotation tailings ranges from 0.015-0.054%, and in the concentrate from 0.23 to 0.72%. The share of oxidized copper is highest in the case of flotation tailings and varies from 10.7 to 25.7%, and in concentrates it is only a few percent. For the multiannual results, the contents of oxidized copper and its shares in enrichment products for all concentrators are clearly higher.
4. Achieving high  $\text{Cu}_{\text{ox}}$  recoveries (over 50%) in technological circuits of KGHM Polska Miedź S.A. concentrators, which are not adapted to the recovery of oxidized copper, requires further research in order to determine the reasons for this behavior.
5. The low content of  $\text{Cu}_{\text{ox}}$  in the concentrator feed, its significant (up to approx. 70%) recovery during sulfide flotation and rather fine particle of oxide Cu minerals make the prospects of

economic recovery of the remaining oxidized copper part for flotation tailings not very successful.

6. Taking into consideration the way of occurrence of  $\text{Cu}_{\text{ox}}$  and  $\text{Cu}_{\text{tot}}$  in flotation tailings as well as available copper recovery techniques, only hydrometallurgical methods, including bio-methods, may be effective, however the issue of economic profitability of such a project is questionable under the current conditions.

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