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FLOTATION OF SULFIDE COPPER ORE FROM LEGNICA-GLOGOW COPPER BASIN (POLAND) IN PROCESS WATER OF DIFFERENT SALINITIES

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Abstract: The composition of water has a significant impact on the flotation. With the increasing salinity of process waters used at the Division of Concentrator Plant (KGHM Polska Miedz SA), it is necessary to investigate the effect of changes in water composition on the flotation of copper ore components from the Legnica-Glogow Copper Basin area (Poland). In this study, the effect of changing water salinity on the flotation efficiency of copper and organic carbon in sulfide copper ore from the Polkowice Concentrator Plant was investigated. In the study, water taken from the processing plant was used. The mineralization and chloride concentration were 54.5 g/L and 23.46 g/L, respectively. The salinity of the process water was changed by concentrating and diluting water (60, 80, 120, 140%), as well as by adding chloride ions (5 and 10 g/L). Based on the study, it was found that with the increase in mineralization, also the chloride ion content of the water is increased, worse flotation of copper carriers and organic carbon was observed at the cleaning flotation stage. Moreover, it was observed that the more the salinity of the process water is increased, the more the efficiency of the rougher flotation improves – while increasing this salinity, the content and loss of Cu in the tailings from this stage decrease. The obtained research results indicate the need to monitor the salinity level of process waters and their composition and perhaps, in the future, the need for modification in this area.

Keywords**:** *flotation, process water salinity, sulfide copper ore, chlorides, copper*

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1. INTRODUCTION

Froth flotation is based on the separation of hydrophobic particles from hydrophilic particles dispersed in water (Laskowski and Luszczkiewicz 1989; Rao and Forssberg 1997). The flotation process belongs to physicochemical methods of separation and its efficiency and selectivity strongly depends on electrochemical interactions between particle / aqueous solution / bubble. The mineral surface charge is affected by the electrolyte type and solution ionic strength, as well as concentration (Hirajima et al. 2016).

The phenomenon of the effect of water salinity on the flotation process is particularly relevant due to the use of seawater in processing in the areas where freshwater access is either impossible or significantly limited. In addition, the accumulation of salts in water results from the recycling of process water (Hirajima et al. 2016; Yepsen et al. 2019). The effect of the presence of various salts in water on the flotation process is a highly complex matter. The favorable effects of salts in flotation slurries were noted as early as the 1930s in the USSR (Ozdemir 2013; Pugh et al. 1997) and these observations were related to coal flotation studies. Later studies have shown that this phenomenon is beneficial only up to a certain maximum salt concentration in solutions – above this limit, the hydrophobicity of coal decreases (Li and Somasundaran 1993). It has been confirmed that the presence of electrolytes in water has an effect on particle-gas bubble interactions (Quinn et al. 2007; Castro and Laskowski 2011; Huang et al. 2013). It has been shown that the energy barrier against the attachment of hydrophobic particles to gas bubbles in saline solutions is markedly reduced, and thus the probability of flotation of such particles increases (Rattanakawin and Hogg 2001; Liang et al. 2007; Ozdemir et al. 2009; Castro and Laskowski 2011). The presence of some inorganic salts in water has an impact on the size, amount and stability of gas bubbles. It is reported to inhibit bubble coalescence and reduce bubble size, thus improving bubble stability and providing adequate frothing characteristics (Hirajima et al. 2016). It was found that the higher flotation recoveries were attributed to a reduction in electrostatic interactions between the particles and bubbles, as well as to an increase in the collision probability with the higher concentration of smaller and non-coalescing bubbles (Paulson and Pugh 1996; Zhao and Peng 2014). Solutions with higher salt concentrations inhibit gas bubble coalescence by draining the inter-bubble layer more slowly (Castro et al. 2013). In water with the high ionic strength, the smaller gas bubbles form with the greater stability and longer residence time in slurry (Quinn et al. 2007, 2014; Castro and Laskowski 2011). This action is also dependent on the valence of the ions present in the salt solution (Marrucci and Nicodemo 1967; Craig et al. 1993). Thus, aqueous solutions with the higher content of inorganic salts can act as a frothing agent or reduce its consumption (Laskowski et al. 2013; Castro et al. 2013).

Pugh et al. (1997) and Paulson and Pugh (1996) classify the electrolytes that affect the graphite flotation process into three distinct groups. Group A ($LaCl_3$, $MgCl_2$, $MgSO_4$, Na_2SO_4, etc.), which includes electrolytes with small, highly charged and hydrated divalent and trivalent cations with the most favorable effect on the graphite flotation process in the concentration range of 0.02–0.06 (to maximum 0.1) M. Group B includes salts such as NaCl, LiCl, KCl, CsCl, NH_4Cl etc. which have a positive effect on flotation in the concentration range of 0.05–0.1 M, although slightly worse than the electrolytes of group A. Group C (CH_3COONa, $NaClO_4$, $HClO_4$, HCl, H_2SO_4, $LiClO_4$) exhibits a very weak effect on flotation efficiency in the studied concentration range of up to 3.0 M.

In the literature, a number of papers have been exploring the effects of salt on the flotation process. These studies were conducted for various materials. A considerable number of papers concern the effect of inorganic salts on flotation, primarily for naturally hydrophobic substances such as coals or graphite (Laskowski 1969; Pugh et al. 1997; Kurniawan et al. 2011). Similar studies have also been carried out for copper sulfide minerals (chalcocite, chalcopyrite, enargite), galena, pyrite or molybdenite (Hirajima et al. 2016; Yepsen et al. 2016; Cruz et al. 2020; Hwang et al. 2024; Laskowski et al. 2019; Peng and Zhao 2011; Zhao and Peng 2014; Castro 2012). The majority of publications dealing with the effects of salinity on the flotation of copper-bearing ores refer to flotation carried out in seawater and the porphyry copper ores themselves.

The effect of selected anions and cations on the flotation of sulfide minerals has been the subject of a number of studies. It has been found that the addition of NaCl in the process water improves the flotation of chalcocite in the presence of clay minerals, by preventing its adsorption on the sulfide surface due to electrostatic repulsion. The surface of both kaolinite (negatively charged) and chalcocite (positively charged) are neutralized by the cations and anions in NaCl solutions (Zhao and Peng 2014). Castro and Laskowski (2011) noted lower flotation efficiency of chalcocite in seawater than in distilled water and distilled water with NaCl. However, pH of the water was of great importance. When $pH<8$, the flotation efficiency in seawater was low. In the pH range from 8 to 9.5, the recovery of chalcocite increased from a level of 20% at pH 8 to 65% at pH 9. Above pH 9.5, the efficiency of flotation in seawater dropped drastically to 0%. In the case of distilled water and saline distilled water, the flotation was effective of up to pH 11, while it began to decline when pH exceeded this value. The results of the study indicate that salinity has an impact on the flotation efficiency, however, other components dissolved in the water may be more important than salinity. In the other paper, Laskowski et al. (2019) stated that in the flotation of sulfide copper ores with xanthate-like collectors, the xanthate collector is apparently not affected by pulp ionic strength. Veki (2013) studied the flotation of chalcopyrite from Cu-Mo ore in tap water and highly mineralized seawater. The content of dissolved substances in tap water was 0.5 g/L (with SO_4^{2-} ions dominating), and in seawater – 36 g/L (with Cl^- ions dominating). Chalcopyrite flotation efficiency was slightly higher in tap water (copper recovery of 86–89%) than in seawater (81–88%). Again as in the study by Castro and Laskowski (2011), there was a decrease in efficiency after pH 10 was exceeded, however, it was not as significant. The probable reason for this difference was another copper-bearing mineral studied in this work – chalcopyrite, instead of chalcocite (Veki, 2013). Jeldres with coworkers (2015) explained the reason for the decrease in flotation efficiency at higher pH values. In their study, the flotation of Cu-Mo ore from Chile was carried out in tap water, sea water and sea water purified from calcium and magnesium. The calcium content in the sea water was 400 ppm, and magnesium 1 280 ppm. As a result of purification, these values decreased and were 176 ppm for calcium and 190 ppm for magnesium, respectively. Flotation tests were performed at two pHs: 7.6 and 11.5. It was found that by reducing the calcium content of water by about 50% and the magnesium content by about 80% eliminated the negative effect of a higher pH on flotation efficiency (Jeldres et al. 2015). In addition to the effect of pH, which for copper mineral is flotation in saline water is also of great importance. It was found that the effect of salinity on the flotation of chalcopyrite is insignificant, while for chalcocite and bornite, too high salt content reduces flotation (Jeldres et al. 2016). Similar observations regarding chalcopyrite were noted by Alvarez and Castro (1976). As for pyrite, the recovery of this sulfide decreases dramatically with the rise of pH in both seawater and sodium chloride solutions. What should be noted is that, the flotation of sulfide minerals in polymetallic ores is strongly influenced by electrochemical conditions (galvanic effects), which means that the flotation behavior of particular minerals in their pure forms can differ significantly from their flotation in the presence of other sulfides. It has been confirmed that the presence of ions from dissolved sulfides also has an effect on sulfide flotation. For example, the presence of Cu^{2+} ions in the flotation solution contribute to the depression of pyrite and chalcopyrite in 0.5 M NaCl solution, while the flotation of chalcopyrite does not change. Furthermore, Hwang et al. (2024) stated that, the effect of the presence of Na^{+} and Cl^{-} ions in water during chalcopyrite flotation, is dependent on the collector dose (PAX) as well as the amount of NaCl in solution. A favorable effect of the presence of NaCl (at 0.1 and 0.7 M) was found for a PAX collector concentration of 50 ppm. At the higher doses of both PAX and NaCl concentrations in water, flotation results for chalcopyrite dramatically decrease. In conclusion, those different effects of various anions and cations on the flotation of sulfide minerals are not fully understood and explained (Zhao and Peng 2014).

One of the world's largest sediment-hosted stratiform copper deposits is located at the Legnica-Glogow Copper Basin (LGCB, SW Poland). This deposit is unique, polymetallic and complex. The copper occurs in the three lithological fractions: easy--upgradeable but low grade sandstone (0.8–1.5% Cu), fairy-upgradeable carbonate (0.5–1.9% Cu), and the richest in copper and silver but poorly upgradeable clay--dolomitic-bituminous black shale (2.8–8.7% Cu) (Kijewski and Leszczynski 2010; Luszczkiewicz et al. 2012). The main copper minerals are: chalcocite, bornite, chalcopyrite and covellite. In addition, the ore contains carriers of other metals: galena, sphalerite, pyrite with marcasite, enargite and tennantite. Among the non-useful minerals, carbonates, clay minerals with micas and quartz dominate (Kucha 2007; Piestrzynski 2007). The presence of clay minerals and organic carbon in shale, which are easy-to-

-float components of ore, strongly reduces the quality of final flotation concentrates (Konieczny et al. 2013). The ores are processed by the three concentrator plants: Lubin, Rudna and Polkowice, being part of the KGHM Polska Miedz SA complex. The copper ore flotation process uses water, which is a mixture of waters, mainly, from mines and "Zelazny Most" tailings dam, and also from the water treatment plant. In total, about 25.5–26 million m^3 of mine water is circulated in O/ZWR during the year. Besides, about 2 million m^3 of wastewater, also entering the cycle, should be added. The rest of the process water is recirculated from the "Zelazny Most" tailings dam, accounting for 120 million m^3 of water per year. The processing plants use about 150 million m^3 of water per year – about 5 m^3 of water per 1 Mg of the processed ore. In addition to the evaporation process of water from the "Zelazny Most" tailings dam, the excess water from the dam is disposed of in the Oder River (KGHM 2025). The composition of mine water, depending on the area of the deposit and the depth of mining, varies significantly. As the depth of mining rises, the salinity of these waters increases, therefore, the water in the flotation circuits of the KGHM Polska Miedz S.A. processing plants is characterized by high content of inorganic salts which is still growing (Wilk and Bochenska 2003). The salinity of water varies from one concentrator plant to another, which is related to the location of the plant and the composition of mine water in a given area of exploitation. Moreover, at each KGHM processing plant, the method of water preparation (proportions of the various water streams) for the flotation process is different. For example, according to Luszczkiewicz et al. (2015), at the Polkowice Concentrator Plant, the underground water, recycled water from the "Zelazny Most" tailings dam and the water from the water treatment plant are combined in a ratio of 70%:25%:5%. The increase in salinity in those process waters at KGHM ore processing plants has been observed since the plants were established. The most recent data on the composition of the process water at Concentrator Plants KGHM Polska Miedz SA can be found in the paper by Bakalarz et al. (2017). According to data from 2011 (Luszczkiewicz et al. 2011), the content of soluble substances was 23–33 g/L, depending on the processing plant, while in the work of Bakalarz et al. (2017) these contents were between 24 and 43 g/L. The major increase was in chloride ions and sodium ions in each of the analyzed process waters which account for more than 70% of all soluble salts in circulating waters, independently of where that water came from (Luszczkiewicz et al. 2015). In the research of Luszczkiewicz et al. (2011), chloride contents in the process waters ranged from 11,150 mg/L for the Lubin Concentrator Plant up to 19,728 mg/L for the Rudna Concentrator Plant. Bakalarz with coauthors (2017) presented the composition of process water from the Lubin Concentrator Plant, in which the content of chloride ions was already 15,295 mg/L, with the total content of soluble compounds at 32,070 mg/L. Since the beginning of monitoring the composition of these waters, the contents of chloride and sodium ions have been increasing all the time. Moreover, these contents are expected to continue to increase (Luszczkiewicz et al. 2015).

There are few papers that have studied the effect of process water salinity on the flotation of particular copper ore components from the LGCB area (Zmudzinski and Lekki 1967; Kowalska 1976, 1978; Luszczkiewicz et al. 2011; Bakalarz et al. 2017). The effect of salinity, particularly chlorides content, on the flotation of individual lithological fractions of copper ore and selected ore components was studied. For carbonate ore, water salinity is favorable, while for sandstone ore, the higher the water salinity, the worse the results of flotation of copper carriers. For shale ore, the best results were obtained for salinities of 6 and 40 g/L (Zmudzinski and Lekki 1967). Other study has indicated that salinity above 20 g/L has a negative effect on copper mineral flotation while too much dilution of process water reduces the efficiency of flotation (Kowalska 1976, 1978). Also in the work of Bakalarz et al. (2017), a positive effect of the presence of salt in process water on the flotation of sulfide copper ore from Lubin Concentrator Plant (KGHM Polska Miedz SA) noted – the poorest results were obtained for tap water. However, dilution of process water improved the flotation of analyzed components compared to the flotation in process water, including an undesirable component organic carbon. The addition of NaCl to the process water slightly decreased the upgrading parameters. However, it should be noted that the differences in the analyzed individual flotation tests are not significant.

As can be seen, the effect of salinity on the flotation of sulfide copper ore at the Legnica-Glogow Copper Basin had not been well investigated. Based on the available literature, it is difficult to clearly state the positive or negative effect of increasing/reducing the salt content of the process water on flotation results. In view of the predicted continuous increase in the salinity of the process waters in the Division of Concentrator Plants of KGHM Polska Miedz SA, in particular, the increase in chloride content, and their not fully understood influence on flotation upgrading indicators, it is a necessary to carry out this type of studies. It should be noted that there is no current study of the effect of the level of mineralization of process waters on the flotation of current copper ore. This is a particularly important issue given the constant variability in both copper ore and process water composition, which has been invariably observed for years. Therefore, in this study, the influence of the salinity level of process water on the flotation upgrading parameters of selected ore components was investigated. The purpose of the study was to determine the effect of increasing and decreasing the salinity of the process water currently used at the Division of Concentrator Plants of KGHM Polska Miedz SA on the selectivity of copper and organic carbon upgrading during flotation of copper ore from current mining. In addition, due to the predicted increase in chloride content in the process water, assuming the constancy of the composition of the remaining salts, the effect of chloride addition in the form of NaCl on the flotation of this ore was studied. The influence of salinity and chloride ion content on the different stages of flotation (rougher, cleaning flotation stage) was also thoroughly analyzed.

2. MATERIALS AND RESEARCH METHODOLOGY

A series of laboratory flotation experiments were carried out on sulfide copper ore derived from the Polkowice Concentrator Plant (KGHM Polska Miedz SA). Seven multistage flotation tests were conducted. These tests were performed using process water, which was modified in two different ways: it was diluted or concentrated, and chloride ions were added in the form of sodium chloride.

The research material was a represented sample of copper ore from the Polkowice Mine area. Before being subjected to the flotation process, the ore was crushed in two stages: crushed in a laboratory jaw crusher (model: LAB-01-65 produced by ZNT EKO-LAB (Jasien, Poland)), and wet milled in a laboratory ball mill (delivered by Orto Alresa-Alvarez Redondo SA (Madrid, Spain)) to a particle size $P_{90} < 0.071$ mm (80 minutes). The milled ore was the material for flotation experiments. In this sample, copper and total organic carbon (TOC) contents were determined, which were 1.76% and 0.63%, respectively. Based on copper assays in particle size classes, it was found that the copper carriers were nearly 60% accumulated in the finest fraction of particles below 0.020 mm.

Both the milling process of the feed and the flotation test were carried out in appropriately prepared process water, which was collected from the Polkowice Concentrator Plant (KGHM Polska Miedz SA). The characteristics of the process water are shown in Table 1. The water contains 23.46 g of chloride ions in 1 liter, while the mass of the dry residue after evaporation of the same volume of water was 54.5 g. Analyzing the contents of all assayed ions (with the exception of copper ions), a marked increase can be seen in comparison with data from the work of Luszczkiewicz et al. (2015). The content of sodium ions increased twice, a significant increase in the content of Mg^{2+} and Ca^{2+} ions was also observed. The data obtained are consistent with the forecasted mineralization growth trends for these waters.

Modification of the process water consisted in its concentration or dilution by adding distilled water and adding the appropriate amount of sodium chloride (p.a., delivered by STANLAB). In preparing the water for milling and flotation, a salinity calculation of the water in relation to the weight of the dry residue in the raw collected process water (taken as 100%) was applied. The dilution or concentration of the raw process water was 60, 80, 120 and 140% (tests no. 1-2, 4-5). Above 140% relative to the mineralization of the raw process water (above a dry residue of 76.3 g/L), precipitation of salts was observed. The selection of the amount of added chloride ions in the form of NaCl was based on the trend, observed for several years, of increasing contents of these ions in the circulating waters of the concentrator plants of KGHM Polska Miedz SA (Luszczkiewicz et al. 2015; Bakalarz et al. 2017). The amounts of chloride added were 5.0 g/L and 10.0 g/L (tests no. 6-7).

Table 1. pH and composition of process water

Parameter/Component	Unit	Value
pH	–	7.51
Dry residue	g/L	54.5
Na^{+}	g/L	17.3
Ca^{2+}	g/L	2.18
Mg^{2+}	g/L	0.41
Cu^{2+}	mg/L	<0.05
Cl^{-}	g/L	23.46
SO_4^{2-}	g/L	3.26

Gravimetric methods: dry residue, SO_4^{2-}; spectrometric methods: Na^{+}, Ca^{2+}, Mg^{2+}, Cu^{2+}; titration method: Cl^{-}.

The characteristics of all performed flotation tests are shown in Table 2. All of them were conducted in a Denver D12 laboratory flotation machine (produced by Metso) equipped with 1.5 and 2.5 L flotation cells. The air flow rate was regulated during each flotation test using a rotameter. The industrial mixture of sodium ethyl and isobutyl xanthate in proportion of 1:1 and the dose of 80 g/Mg was used as a collector. An aqueous solution of mixture of alkyl polyglycol ethers was utilized as a frother at a dosage of 20 g/Mg in each flotation test. Both reagents were prepared directly before the flotation test. All flotation tests were performed according to the flowsheet shown in Fig. 1. Three concentrates, two middlings and one tailing were collected in each flotation test. All the products were washed in distilled water, dried in 105 °C and weighted. The contents of copper and total organic carbon (TOC) were determined by spectrometric method.

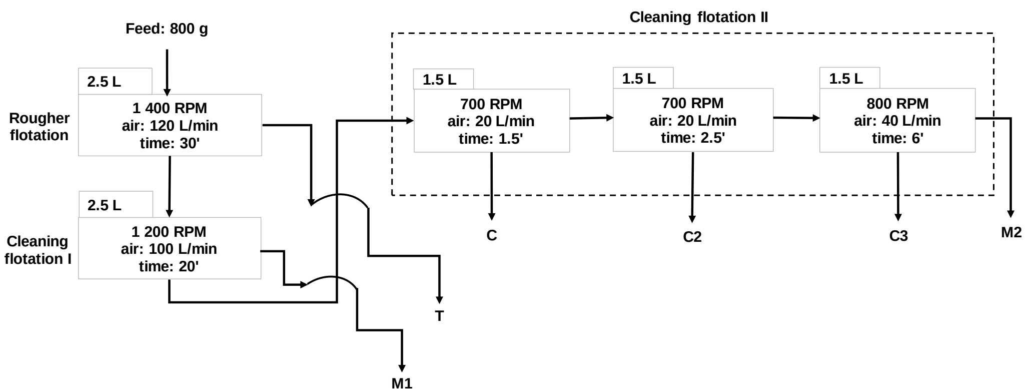

Fig. 1. Scheme of flotation test

The beneficiation balances for the individual ore components were calculated, and based on them, grade-recovery upgrading curves and kinetics curves were prepared.

Table 2. Characteristics of flotation experiments

Test no.	Degree of dilution or concentration of process water [%]	Dry residue [g/L]	Mass of NaCl added per 1 L of water [g]	Content of chloride ions [g/L]	Percentage of chlorides in the dry residue [%]
1	60	32.7		14.08	
2	80	43.6		18.77	
3	raw	54.5	–	23.46	43.05
4	120	65.4		28.15	
5	140	76.3		32.84	
6	–	64.1	9.64	28.46	44.40
7		72.4	17.88	33.46	46.22

Test using the process water currently used in Polkowice Concentrator Plant was highlighted.

3. DISCUSSION

The obtained results were divided and compared in two series. First, the effect on the results of copper ore beneficiation of the concentration/dilution of the process water collected from the Polkowice Concentrator Plant was analyzed, and then the addition of sodium chloride to this process water was analyzed.

Figures 2a–d show the flotation results of the two analyzed components in process water with different mineralization. Based on these data, it can be observed that the course of both grade-recovery upgrading and kinetics curves for copper in flotation tests using process water with mineralization levels of 32.7, 43.6 and 54.5 g/L are similar to each other (Figs. 2a, b). However, it can be seen that increasing the mineralization of process water results in a decrease in the content of this metal in the concentrates received at the cleaning flotation stage, which is a negative trend. In addition, it can be noted that an increase in water salinity improves the flotation rate of copper carriers. Similar observations were noted for total organic carbon (Figs. 2c, d). Organic carbon under conditions of higher water mineralization (65.4 and 76.3 g/L) flotation is noticeably worse at the cleaning flotation stage. The higher the mineralization of the water used in flotation, the lower the content of this undesirable component in the concentrates, which is a favorable phenomenon. Studying the course of kinetics curves for TOC, it can be seen that the increased mineralization of waters promotes the better flotation kinetics of carriers of this component.

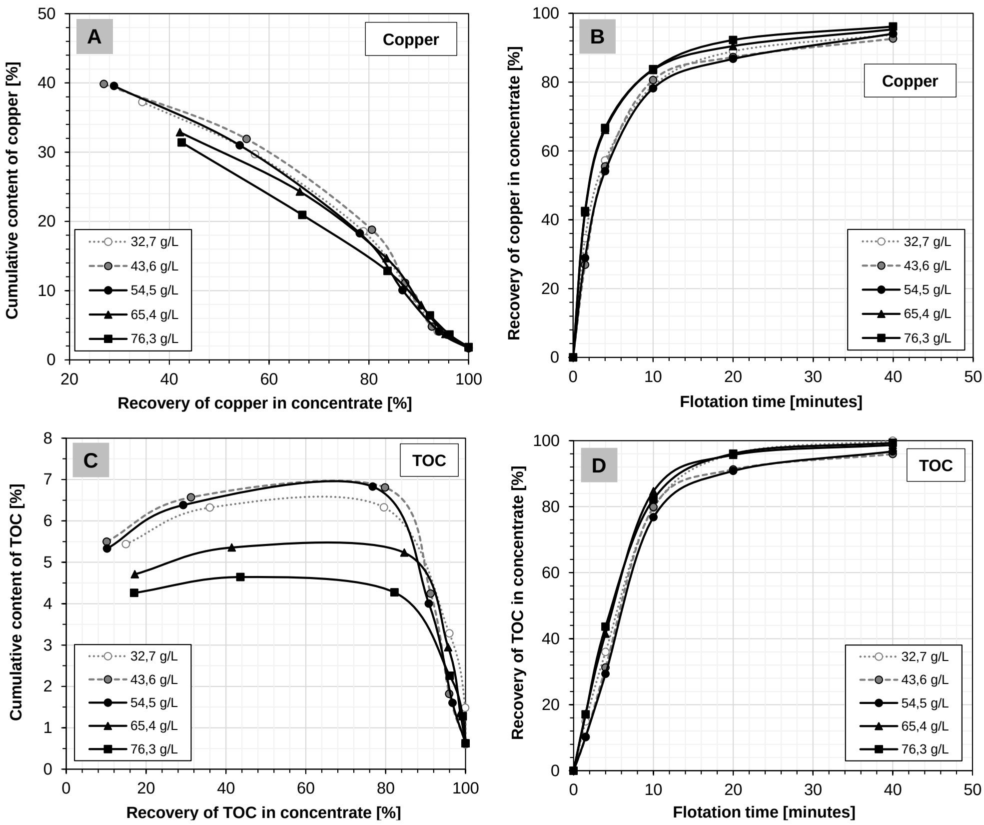

Fig. 2. Results of ore flotation according to copper (A-B) and TOC (C-D) balance in different salinity of process water

The effect of chloride ion addition to process water on copper flotation and TOC is shown in Figures 3a-d. The results of the flotation tests with the addition of NaCl were compared with the copper ore flotation in process water currently used at the processing plant. As was the case with flotation in the previous series, the addition of chloride ions in the form of NaCl also markedly reduced the quality of cleaning flotation concentrates in regard to metal content. The reduction in organic carbon content at higher chloride contents in water is a desirable effect. Similar observations were noted for the flotation rate: the higher the chloride content, the higher the flotation rate of the analyzed components. Moreover, comparing the shape and the position of the TOC curves for flotation tests 4 and 6, as well as 5 and 7 (Figs. 2c, d and 3c, d), it can be seen that the flotation of this useless and undesirable component in water with the addition of NaCl is better than in concentrated water with similar chloride ion contents. Such a phenomenon was not observed for the copper-bearing minerals.

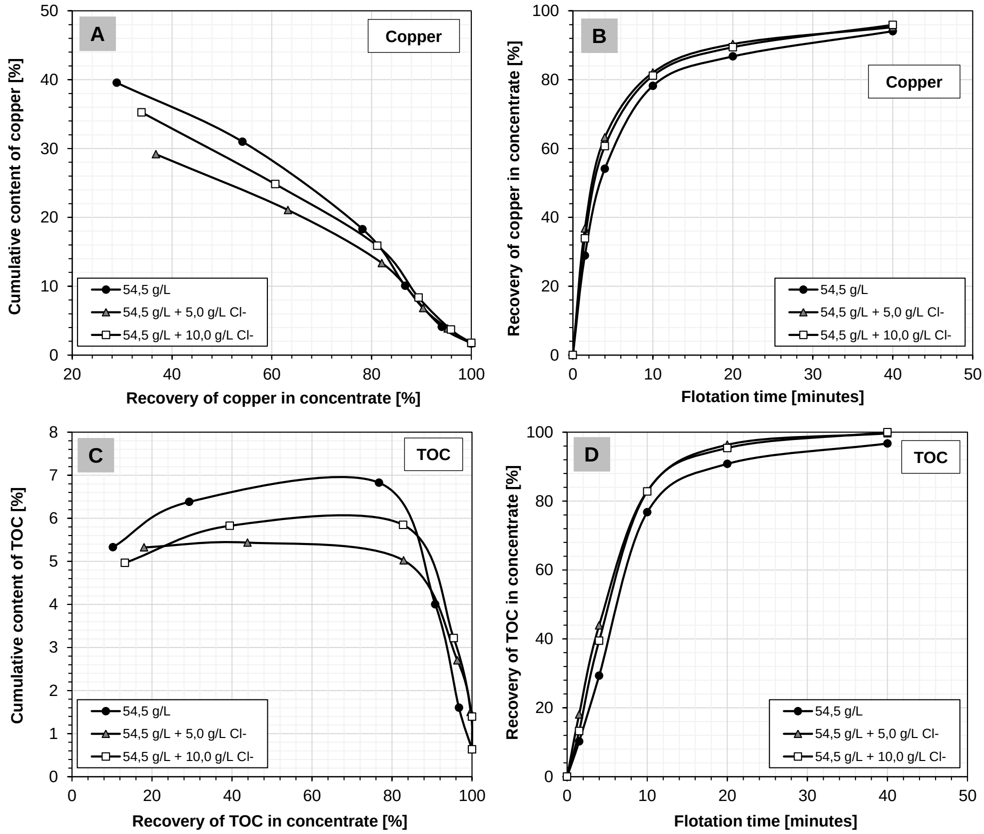

Fig. 3. Results of ore flotation according to copper (A-B) and TOC (C-D) balance in process water with different chloride contents

Table 3. Characteristics of flotation tailings: yields, contents and losses of analyzed components

Test no.	Dry residue (in 1 L of water) [g]	Content of chloride ions [g/L]	Yield of tailing [%]	Cu		TOC	
				Content [%]	Loss [%]	Content [%]	Loss [%]
1	32.7	14.08	59.52	0.18	6.18	0.00	0.06
2	43.6	18.77	66.88	0.19	7.36	0.04	4.09
3	54.5	23.46	61.63	0.16	5.91	0.03	3.27
4	65.4	28.15	54.14	0.15	4.65	0.02	1.31
5	76.3	32.84	51.45	0.14	3.82	0.01	0.68
6	64.1	28.46	57.21	0.14	4.74	0.00	0.32
7	72.4	33.46	54.40	0.13	4.09	0.00	0.00

Test using the process water currently used in Polkowice Concentrator Plant was highlighted.

The study showed a clear negative effect of the increase in salinity of the process water as well as the addition of chloride ions on the flotation of copper carriers in the final stage of the flotation test, the second cleaning flotation. Nevertheless, the tailings from the rougher flotation, which are characterized by the highest yield and thus significantly determine the efficiency of the flotation process (irreversible metal losses in the tailings deposited in the tailings dam), were also analyzed. Table 3 shows the characteristics of the rougher flotation tailings from each test conducted in this paper.

As can be seen in Table 3, the mineralization and chloride content in the process water affect the content of copper and its loss in these tailings. Figures 4 and 5 show these correlations. As can be noted, the higher the salinity of the water and chloride content, the lower this precious metal content in this tailing and its loss in this product. Moreover, higher water recovery and more stable froth were observed during flotation with higher salinity waters during the rougher flotation. These observations are consistent with the data from Johnson (1972), Laplante et al. (1989) and Troncoso et al. (2014). Johnson (1972) and Laplante et al. (1989) stated that the increase in froth stability and higher water recovery during flotation in saline waters results from the mechanical entrainment of the fine gangue minerals. In the case of Polkowice ore, the non-useful components are mainly carbonates, quartz and clay minerals. Moreover, fine non-useful particles, such as quartz, can go through not only mechanical entrainment but also flotation. Troncoso et al. (2014) showed that the contact angle of quartz increases with the boost of salt concentration (e.g., NaCl, $CaCl_2$, and $AlCl_3$). This means that the reason for the higher copper recoveries in the concentrate from the rougher flotation, and therefore a lower loss of copper in the tailings from this stage, apart from the better flotation kinetics of copper-bearing minerals, could be the flotation of intergrowths of gangue with useful minerals. The presence of intergrowths of non-useful minerals with sulfides, including the finest particle size classes of copper ore subjected to flotation at the Division of Concentrator Plant of KGHM has been confirmed in numerous works (e.g. Ostrowski et al. 2019; Bakalarz et al. 2017; Bakalarz 2019). This is a significant finding in terms of the amount of flotation tailings directed to the "Zelazny Most" tailings dam (approximately 28 million tons per year) and the total loss of copper in this stream (about 57,000 tons of copper per year) (Bakalarz and Duchnowska 2024). The observed phenomenon is beneficial in the case of rougher flotation (reducing the loss of valuable metals in the final tailings) while in the cleaning stage flotations it causes a decrease in the quality of final concentrates. According to the latest data available in the literature (Kubik et al. 2018), copper ore from the Polkowice Concentrator Plant is characterized by mineralization with a predominance of chalcocite and significantly lower contents of other copper-bearing sulfides (bornite and chalcopyrite). It was mentioned before that flotation of both chalcocite and bornite in water with high salt content is significantly poorer (Jeldres et al. 2016). In addition, the quality decrease in final concentrates (the last cleaning flotation) is probably due to the coating of useful minerals by clay minerals. Numerous studies have shown that a higher concentrations of electrolytes (chloride, sodium, calcium, magnesium) in process waters tend to promote clay coatings, which reduces sulfide floatability (Cruz et al. 2020; Hirajima et al. 2016; Zhao and Peng 2014). Nevertheless, the total copper recovery in the concentrates from the last cleaning flotation increases as the mineralization of the water grows.

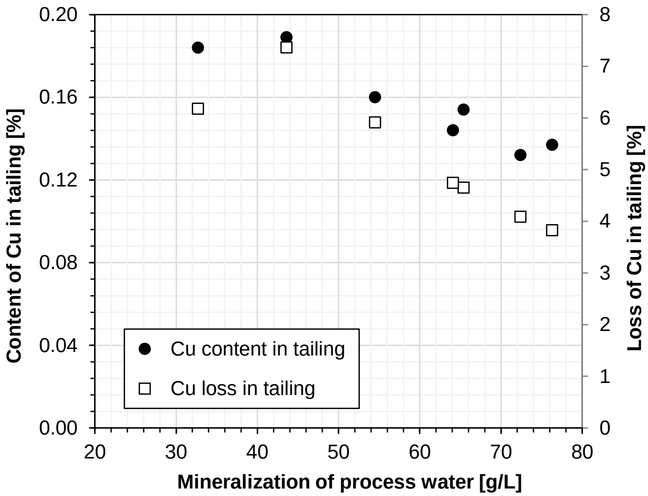

Fig. 4. Change in Cu content and loss in tailings from rougher flotation in the water with different mineralization

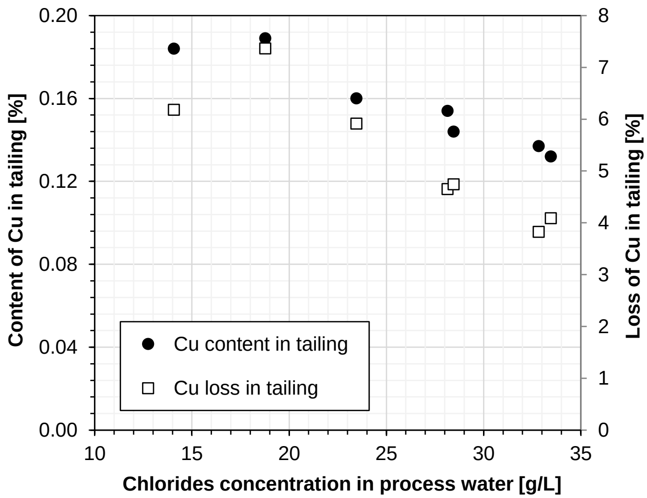

Fig. 5. Change in Cu content and loss in tailings from rougher flotation in the water with different chlorides content

As can be seen, the effect of the presence of higher concentrations of NaCl in water in the flotation of sulfide minerals is not fully understood. Nevertheless, it is clear that the presence of these ions has a beneficial effect on sulfide flotation, however, only up to a certain concentration. In view of the continued increase in the salinity of KGHM's process water, its negative impact on upgrading parameters is also to be expected, especially for the final copper concentrates. The results obtained in this study indicate that under the conditions of forecasted increases in the chloride content of the process waters, it is recommended to take steps to reduce the ionic strength in the waters at the final stages of upgrading. In addition, it is difficult at this stage to determine the effect of individual ions on the flotation of both metal carriers and non-useful components such as total organic carbon, due to the complex chemical and unstable composition of the process water at KGHM. It should be noted that the received results can also be affected by increased or decreased concentrations of other ions, such as Cu, Ca, Mg or Fe. What is important is the need to monitor the composition of the process water at the Division of Concentrator Plant, because as the studies show, the composition of this water has a significant impact on the quality and quality parameters of the final products from beneficiation.

4. SUMMARY AND CONCLUSIONS

The efficiency of the flotation process strongly depends on the composition and qualities of the water used in the beneficiation process. The presence of inorganic electrolytes which dominate the process water is of particular significance. The water used at the Division of Concentrator Plant (KGHM Polska Miedz SA) is a mixture of the underground water pumped out of the mines, water returned from the landfill and from the water treatment plant. Over several decades of operation, the salinity of the mine water has increased markedly and, according to current forecasts, the increase in salinity of the process water will continue due to further increases in the mining depth.

The study showed that both the increasing and decreasing of the mineralization of the process water used at the Polkowice Concentrator Plant has an influence on copper and organic carbon upgrading parameters. An increase in the water mineralization in relation to the water currently used at the plant (dry residue: 54.5 g/L, Cl^-: 23.46 g/L) results in a decrease in the quality of concentrates obtained at the cleaning flotation stage – lower copper contents in these products were obtained. At the same time, a decrease in the flotation of organic carbon at this stage of flotation was observed, which is a positive phenomenon. As a result of the increase in the mineralization of the process water, also the chloride content in this water, the quality of the rougher flotation tailings is improved – lower copper contents in the tailings were obtained, resulting in the lower losses of this metal in this final product. In addition, an increase in water salinity improves the flotation kinetics of both Cu and TOC, which is particularly evident in flotation in the process water with the highest mineralization (more than 60 g/L) and in flotation in the water with the addition of chloride ions.

The results obtained in the present study confirmed the influence of the mineralization degree of process waters on the upgrading process of sulfide copper ore from LGCB. It seems to be necessary to monitor the composition of the process water at Division of Concentrator Plant of KGHM PM SA, and perhaps to modify its composition in the future, as studies show that the water composition has a significant impact on the quality and quality parameters of the final products from beneficiation.

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