

The effect of process water salinity on flotation of copper ore from Lubin mining region (SW Poland)

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Abstract. The process water used for the flotation of sedimentary copper ore in ore concentration plants in KGHM Polska Miedz S.A. were characterized. The process water used in the flotation circuits is heavily saline. It contains between 25 and 45 g/dm³ of soluble components, and the main constituent, in about 75%, is NaCl. Process water used for flotation consists of reclaimed water from the tailing dam and mine water. The effect of process water salinity on the processes of copper flotation from the Lubin mine area was described. The results of laboratory flotation experiments conducted in tap water and in water of different salinity levels were compared. The effect of the salinity of water within specified concentration limits was generally found to be beneficial for upgrading of the examined ore.

1 Introduction

1.1 The effect of process water salinity on the flotation processes

The physicochemical properties of the process water, i.e. its ionic composition and the amount of dissolved substances, are one of the most important factors influencing the course of flotation processes. It is known from industrial practice that the concentration of soluble salts in flotation slurries affects the course of flotation processes. Because of the widespread freshwater shortage in industrial areas, the use of saline water in the flotation process is a necessity. Since the 1930s saline sea water has been used for flotation [1]. Laskowski [2] described the beneficial effect of salts soluble in flotation solutions on the course and effectiveness of flotation. This was, however, mainly related to naturally very hydrophobic minerals and hard coal. In such raw materials there is a 2-3 times increase in flotation rate compared to non-saline water. Pugh et al [3] groups electrolytes that affect the efficiency of graphite flotation into three groups. Group A electrolytes of small, strongly charged and hydrated cations (divalent and trivalent), such as MgCl₂, CaCl₂, Na₂SO₄, MgSO₄, LiCl₃ have the most favourable impact. In the presence of these cations, the flotation occurs at a concentration of 0.02 M and reaches the maximum at a concentration of approximately 0.06 to 1.0 M. Group B, comprising NaCl, LiCl, KCl, CsCl, NH₄Cl, shows the most favourable, however, slightly weaker effects on flotation at concentrations from 0.05 to 0.1 M. The last, C group of electrolytes (NaClO₄, HClO₄, HCl, H₂SO₄, LiClO₄, CH₃COONa) has a very poor effect on the flotation recovery and effectiveness substantially regardless of the concentration measured to

approximately 3.0 M. The effect of the mentioned mono- and divalent metal salts in sulphide minerals flotation differs considerably. Many scholars have unambiguously stated that in the case of chalcopyrite monovalent metal salts, e.g. NaCl and KCl, have a beneficial effect on flotation upgradeability. The presence of calcium and magnesium salts, on the other hand, causes respectively a weak and strong effect of the depression of flotation of this mineral [4,5]. Many authors point to the beneficial effect of sulphides flotation in saline water against low mineralization waters, e.g. tap water [6].

Flotation of metal ore in saline water has been the subject of many studies conducted in recent years due to the increasing shortage of freshwater or lack of it in major mining areas, especially of non-ferrous metal ore. The described problems most often concern the use of seawater and, in general, closed circuit water including water recycling from thickening and filtration of the concentrate and, first of all, from the system of processing plant – settling pond of flotation tailing [7]. The quoted authors recommend ongoing monitoring of the physicochemical state of circulating water, e.g. ionic composition, Eh-pH potential, suspended colloidal particles, and the adapting of the technological regime to changing water properties.

The effect of process water salinity on the processes of flotation of ores mined in Lubin Mining Region has been observed since the start of the concentrating plants operation. From the study of Zmudzinski and Lekki [8], analyzed by Karpisz with upgrading curves [9], it results that the artificial addition of NaCl to tap water up to 100 g/dm³ has a positive influence on the flotation of carbonate and shale ore, while the addition above 6 g/dm³ adversely affected the flotation of sandstone ore. In the studies of Kowalska [10,11], the influence of dilution of

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process water of Polkowice Concentrator with low-saline water collected in those days from the Odra River was found to be unfavorable.

The problem of the effect of process water salinity on the flotation process was also recently investigated by Luszczykiewicz and co-workers [12]. The studies have shown that dilution of process water does not alter the results or leads to improvement of flotation efficiency. By contrast, increasing of salt concentration of process water by evaporation results in a significant deterioration of the flotation efficiency. In turn, the purification of process water with the use of activated carbon most often also leads to a deterioration in the selectivity of flotation. The deliberate addition of NaCl to process water in a very different way influenced the results of flotation. This generally did not change the selectivity of Cu and C_{org} flotation but slightly decreased the flotation selectivity of Ag and Pb.

1.2 Water used in technological processes of ore upgrading in KGHM Polska Miedz S.A.

The process water used in ore upgrading in KGHM Polska Miedz S.A. consists of reclaimed water from the tailing dam which is fed with mine water. The latter significantly differs in the amount of the soluble components in the particular mining areas associated with processing plants. Water circulating in concentrating plants is additionally supplied with soluble components washed out of the treated ores. As a result, water in the flotation circuits of the KGHM Polska Miedz S.A. processing plants is characterized by high content of inorganic salts. According to Luszczykiewicz and others [12], the concentration of soluble components in recycled water from the Zelazny Most tailings dam, which feeds predominantly flotation systems, varies within 23–33 g/dm³. The recycled water from the "Zelazny Most" pond is mixed with mine water in the processing plants, carrying different amounts of soluble salts, therefore, in different areas of the Concentrator, flotation process water varies and, depending on the region, contains between 20 and 40 g/dm³ of soluble components (Table 1).

As noted in the study of Luszczykiewicz et al. [13], data from Table 1 show that the ionic product of calcium and sulphate ions is $0.77 \cdot 10^{-3}$ up to $1.2 \cdot 10^{-3}$ and it is significantly higher than the solubility equilibrium product of various forms of calcium sulphate (below $3.1 \cdot 10^{-5}$). This means that the KGHM process water is supersaturated with calcium sulphate (gypsum and anhydrite) and precipitation of these substances is expected. This supersaturation is based on the presence of other salts that shift chemical equilibrium and the so-called activity coefficients and thus solubility. The source of sulphate ions, besides gypsum or anhydrite, is also magnesium sulphate. The $MgSO_4$ stoichiometry ($SO_4^{2-} = 96$ g/mol, $M_{Mg^{+2}} = 24.3$ g/mol, $M_{MgSO_4} = 120.3$ g/mol) shows that if in process water of the Concentrator is at least 250 mg/dm³ Mg^{2+} this is accompanied by about 1000 mg/dm³ sulphate ions. In turn, the discussed water contains approximately 3000 mg/dm³ SO_4^{2-} ions, i.e. 2000

mg/dm³ comes from $CaSO_4$ (theoretically approx. 1700 mg/dm³).

Table 1. Results of determination of the major chemical components of process water of the Lubin, Polkowice and Rudna Concentrators [13].

Symbol	unit	Lubin	Polkowice	Rudna	
Fe	mg/dm ³	0.22	0.66	0.61	
Cu	mg/dm ³	0.202	4.80	2.02	
Zn	mg/dm ³	0.168	0.320	0.672	
Pb	mg/dm ³	<0.005	0.478	1.50	
As	mg/dm ³	<0.005	0.038	<0,005	
Mg	mg/dm ³	265	253	121.50	
	mol/dm ³	0.011	0.010	0.005	
Ca	mg/dm ³	1325	1614	994	
	mol/dm ³	0.0330	0.0403	0.0248	
Na	mg/dm ³	6 162	7 827	12 171	
	mol/dm ³	0.268	0.340	0.529	
SO ₄ ²⁻	mg/dm ³	2 810	2 829	2 994	
	mol/dm ³	0.0293	0.0295	0.0312	
Cl ⁻	mg/dm ³	11 150	13 438	19 728	
	mol/dm ³	0.315	0.379	0.556	
Soluble components	mg/dm ³	24 180	29 820	43 450	
Total suspended matter	mg/dm ³	9.0	18.0	56.0	
Dry residue	mg/dm ³	24 440	29 690	41 330	
Dry residue	CaO	%	4.44	4.71	3.58
	MgO	%	1.19	1.28	1.04
	NaCl	%	74.82	86.04	62.43
Na+Cl in dissolved components	%	71.6	71.32	73.4	

Groundwater (mine water), depending on the area of the deposit and the depth of the mining, varies considerably. Kleczkowski et al. [14] report that the increase in mineralization (dry residue after evaporation) is observed with depth. Mineralization in the mining areas of the deposit in years 2003–2006 in the southern areas ranged from 0.79 to 4.25 g/dm³ on average 2.12 g/dm³, while in the northern areas from 22.55 to 328.80 g/dm³. The average mineralization of water in this area in the region of the deepest mining works is approx. 161 g/dm³ including concentration of chlorides over 100 g/dm³. In the NE direction with depth, the mineralization increases even to more than 330 g/dm³. The increase in mineralization is related to the increase in chlorides, since the concentration of sulphate already at a depth of about 600 m is stabilized at about 2 g/dm³. The water in the northern area of the deposit is saline of type Cl-Na-Ca, in which the presence of iodides and bromides and significant amounts of iron are found. In the southern areas there is saline of type SO₄-Cl-Ca and SO₄-Cl-Na [14].

Process water used in flotation in different regions of the concentrating plant differs in composition. This is due to the fact of mixing of recycled water from the tailing dam with mine drainage water, which in the particular

mining areas varies in both amount and concentration. As shown in Table 1, the salinity considered as the amount of substances dissolved in water varies between 24 and 43 g/dm³ depending on the Concentrator's connected with the mining area. The dominant components of this water are Na⁺ and Cl⁻ ions, therefore, the main component is sodium chloride, whose share in total water salinity in all three plants is similar, at 71–73%. The calcium and sulphate ions present in the process water are mostly derived from the dissolution of the anhydrite found in the ore. The sulphate concentration is maintained at a constant level of 3 g/dm³. The source of sulphate ions is also magnesium sulphate.

The analysis of salt content in process water in all three regions of the Concentrator observed over many years shows that chlorine concentration in process water has been steadily increasing [12].

The increase in salinity of flotation water has been observed since the beginning of the development of the Lubin-Glogow Copper Basin (LGOM) deposits. The salinity is systematically increasing from around 6 g/dm³ of soluble substances in reclaimed water from the settling pond "Gilów" [15] to the present amount of approx. 35–40 g/dm³. Currently, in the reclaimed water of the "Zelazny Most" tailings dam, compared to data from the late 1960s, the content of soluble components and chloride ions increased approximately fivefold/sixfold and the amount of sulfate ions increased more than one and a half times with a tendency toward equilibrium at approx. 3000 mg/dm³.

2 Experimental

2.1. Research materials and methodology

The research material was a sample of ore from the Lubin Mine area. The ore sample represented crushed raw feed from current production. It was collected from the Lubin Concentrator's carbonaceous ore stream, directed to the 1st stage of grinding. The sample was crushed in a laboratory jaw crusher to a grain size <1 mm and subjected to grinding in a laboratory to a grain size P₉₀<0.071 mm (Table 2). The ground ore was the material for flotation experiments. Chemical analyzes showed the following content of balanced components: 0.97% Cu, 50 g/Mg Ag, 0.99% C_{org}.

The composition of process water used in the flotation experiments, taken from the plant technological circuit during the collection of test ore, is summarized in Table 3. Table 3 also contains the composition of tap water used in experiments.

The experiments were performed in a laboratory Mechanobr type flotation machine with 1 dm³ cell volume. Standard flotation reagents used in the Lubin Concentrator were used in the experiments: the collector was sodium ethyl and isobutyl xanthate, mixed with Hostafлот LET at 80:20, dosed at 74 g/Mg of the ore; a mixture of Corflot with Nasfroth in ratio 40:60 in the amount of 16 g/Mg was used as frother.

Table 2. Particle size analysis of feed for flotation experiments.

Grain class, mm	Yield, %	100-Σ%, %	Cu		Ag	
			λ, %	ε, %	λ, g/Mg	ε, %
> 0.100	2.5	100.0	0.56	1.4	60	3.1
0.071 ÷ 0.100	7.4	97.5	0.62	4.8	36	5.5
0.040 ÷ 0.071	25.0	90.1	0.93	24.2	44	22.7
0.020 ÷ 0.040	21.7	65.0	1.16	26.2	40	17.9
<0.020	43.3	43.3	0.96	43.3	57	50.8
Calculated feed	100.00		0.96	100.0	49	100.0
Assayed feed			0.97		50	

λ – component content in the product, %

ε – component distribution in the product, %

Table 3. Results of chemical analysis of process and tap water used in flotation experiments.

Component	Content mg/dm ³	
	Process water	Tap water
Total iron	<0.05	<0.02
Copper	0.028	not found
Zinc	0.096	not found
Lead	0.013	not found
Arsenic	<0.005	not found
Magnesium	394	13.3
Calcium	1687	93
Sodium	8866	22.3
Sulphates	2962	105
Nitrates	35.9	17.7
Nitric nitrogen	8.12	not found
Chlorides	15295	49.8
CaCO ₃	5839	288
Soluble components	32070	350
Dry residue	32320	

The experiments were performed according to the flowsheet shown in Fig. 1. Four series of tests with different types of water were made:

- with natural process water taken in the Lubin Concentrator where the ore material came from (Table 3). This water contained approx. 32 g/dm³ of dissolved components,
- with process water diluted with tap water in the proportion of 30% of process water and 70% of tap water. This water therefore contained approx. 10 g/dm³ of dissolved components,
- with process water, in which pure sodium chloride was additionally dissolved. The amount added was equal to 100% of the amount of this salt present in the natural state in process water. The content of NaCl in the natural state of process water was calculated stoichiometrically assuming that the total Cl⁻ ion is bounded in the form of NaCl. 18.4 g/dm³ of crystalline NaCl was added to natural process water, resulting in its total content of 43.9 g/dm³ of soluble components, including 37.8 g/dm³ of dissolved NaCl,
- with tap water.

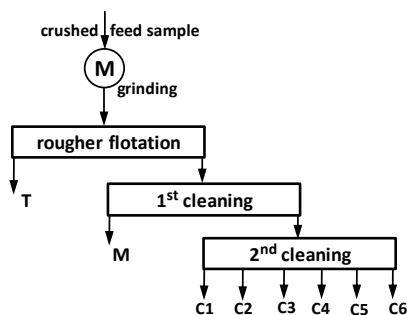


Fig. 1. General flowsheet of flotation experiments.

2.2. Discussion of results

Fig. 2-4 show the results of the flotation experiments of the examined ore in the form of recovery-grade and recovery-recovery upgrading curves obtained in various types of water, balanced for copper, silver and organic carbon.

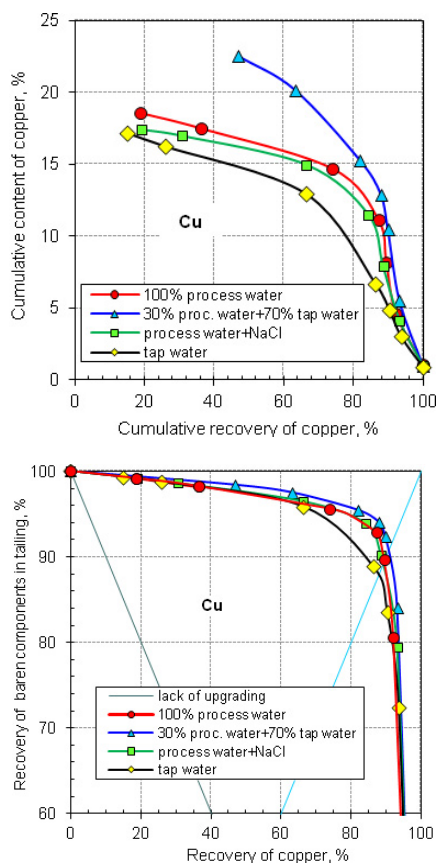


Fig. 2. Results of ore flotation according to Cu balance in different types of water.

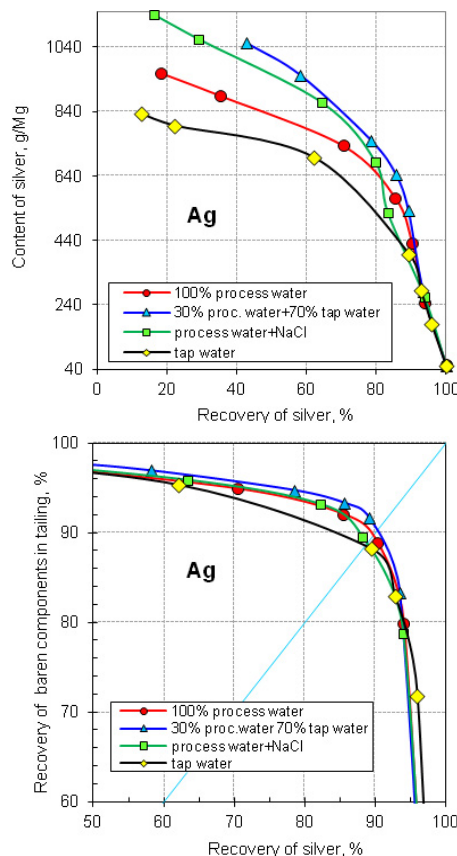


Fig. 3. Results of flotation experiments balanced by silver

Analysis of upgrading curves showed that water salinity has a positive effect on the floatability of all three balanced components. The worst results of the process is observed in the case of tap water. With the increase of salts dissolved in the flotation water (30% of the saline process water with 70% of tap water) used in the tests, the results of upgrading were most favorable in the series of tests described. Flotation in the naturally saline process water was significantly worse than flotation in diluted process water, but significantly better than in tap water. Increasing the salinity of process water by dissolving NaCl in it, slightly affected the results of flotation according to the Cu balance (Fig. 2). In contrast, this addition had a better effect on silver upgrading (Fig. 3). By comparing the floatability of copper and silver in all four types of water (Fig. 5), one notices a slightly worse silver upgradeability. With the increase in salinity (NaCl addition) these differences become smaller.

Upgrading of organic carbon as an unfavorable component in copper concentrates (Fig. 4) shows a downward trend with increasing water salinity in flotation. The strong increase in salinity, however, causes a significant increase in the content of this component in the obtained concentrates. Comparison of the behavior of organic carbon in the analyzed water types (Fig. 5) clearly indicates that this component is the worst upgraded in tap water, and any increase in salinity has a positive effect on its flotation.

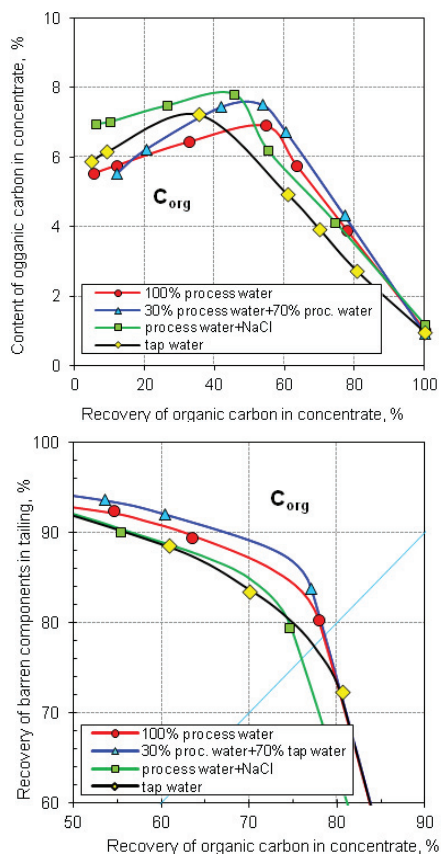


Fig. 4. Results of flotation experiments balanced by organic carbon.

The results of copper ore flotation experiments in flotation water of different salinity levels have been confirmed by numerous literature data on the effect of sea water on the efficiency of upgrading of these ores. The copper ore from the Lubin Concentrator used in experiments is of the polymineral character. The metal carriers in this ore are mainly bornite, chalcopyrite and to a lesser amount chalcocite. Mineralogical analyzes of flotation products indicated a beneficial effect of salinity on the upgrading of chalcopyrite and bornite in the concentrate, whereas chalcocite clearly exhibited poorer floatability. It can be assumed that the mechanism of the beneficial effect of salinity on the flotation of sulphide minerals is in accordance with the literature [5,6]. In case of presence of clay minerals in the flotation suspension Zhao and Peng [16] explain the deterioration of water flotation in tap water by the electrochemical impact of mineral surface resulting in easier mulching in tap water on sulphide minerals, especially on chalcocite.

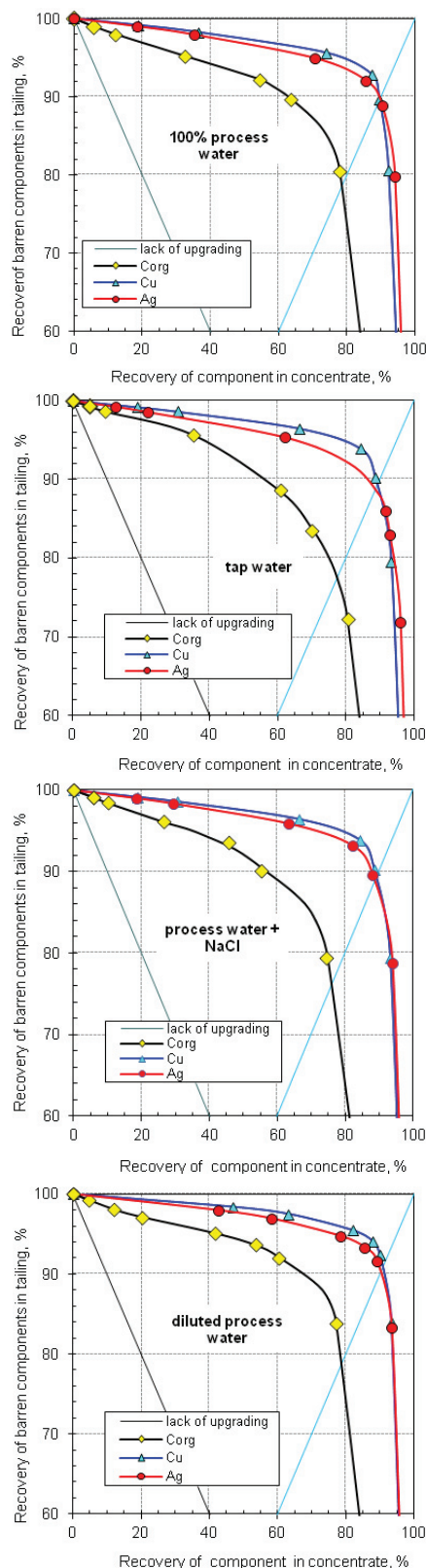


Fig. 5. Comparison of the results of flotation experiments in the analysed types of water.

3 Conclusion

The balances of flotation experiments of copper ore from the Lubin mining region, analyzed in terms of copper, silver and organic carbon indicate the beneficial effect of the salinity of the water used on the upgradeability of the balanced components. Dilution of process water with tap water in a ratio of 70 to 30% resulted in the most favorable flotation conditions for all balanced components: copper, silver and organic carbon. Flotation in process water indicates more favorable flotation effects of all balanced components compared to flotation in tap water.

When comparing the flotability of copper and silver in all four analysed types of water, a slightly weaker silver upgradeability is noted. With the increase in salinity (NaCl added at 100% of its original amount in process water), these differences become smaller. On the other hand, the disadvantage of organic carbon is that it is poorly upgraded in tap water, and any increase in salinity has a positive effect on its flotation.

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