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EFFECT OF NON-OXIDATIVE LEACHING ON FLOTATION EFFICIENCY OF LUBIN CONCENTRATOR MIDDLINGS

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Mineralogical and petrological properties of black shale occurring in the copper ore deposit of the Foresudetic Monocline have been described. Specific character of the shale layer and its behaviour in the ore processing technology was discussed. A concept of recovery of the black shale from flotation circuits of the Lubin Concentrator by separating a by-product (middlings), which represents the tailings of the first cleaning flotation was presented. It was found that the investigated by-product cannot be practically upgraded using standard xanthate flotation. This is due to a remarkable enrichment in the organic carbon, similarly to the content of carbon in petrographically "pure" black shales. After a comprehensive examination it was assumed that the Lubin middlings can be regarded as a shale concentrate ready for bio- and hydrometallurgical processing. The effect of non-oxidative leaching of middlings with sulphuric acid on further flotation was presented. It was shown that nonoxidative leaching is a selective process, in which calcium and magnesium carbonates decomposition leads to effective liberation of sulphide minerals finely disseminated in hydrophilic gangue. Partial carbonates removal (between 70 and 90% of the total carbonates content) from the middlings resulted in evident liberation of valuable minerals. Consequently, it resulted in an increase of both recovery and the content of metals in concentrates obtained by flotation of shale by-product after non-oxidative leaching.

Key words: copper ores, black shale, flotation, non-oxidative leaching

INTRODUCTION

Black shale fraction in the copper ore deposit of the Foresudetic Monocline is one of the three, next to sandstone and carbonate, copper-bearing lithological layer distinguished in the exploited copper ore in the Legnica-Glogow basin (LGOM). From

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the lithological and geochemical points of view the copper ore is of very specific and unique composition, which require specific technology for processing of the mined ores.

The shale series, called the copper-bearing shale, forms in the deposit layers of thickness from 0.3-0.8 to 1.7 m. It is a heterogeneous material, mainly consisting of bituminous shale, which basic components are clay minerals, carbonate minerals (dolomite and calcite), organic substance (mainly of sapropel origin) and detritic material (Konstantynowicz-Zielinska, 1990). Dark or black color of the shale is considerably related to the presence of carbonaceous organic matter.

In the whole area of the LGOM deposit three shale layers can be distinguished: black clay shale, clay-dolomitic, and dolomitic-clay (Rydzewski, 1996). Shale ore, considering its high copper content (on average from several to a dozen percent) and valuable accompanying metals and compounds, is believed to be the most valuable among all lithological layers of the LGOM deposit. Tomaszewski (1985), calling the shale ore "natural polymetalic concentrate", estimated that black shale present in the deposit is the carrier of about 25 % of the copper reserves and about 30-40 % of copper accompanying metals. Kijewski and Jarosz (1987) assessed that bituminous shale includes 5-8 % of the ore resource in the deposit. The shale ore is recognized as the most difficult-to upgrade part of mixed ore directed to concentrators in comparison with sandstone and carbonate fraction of the ore. Fine disseminated sulphide minerals present in the clay and clayey dolomitic matter occur as intergrowths with carbonaceous substance. Hard liberation of fine particles of copper minerals during standard grinding process of the shale is the main cause of its upgrading difficulties by flotation.

As a result of the method of exploitation of the deposit, which are currently used, the shale ore is processed in the copper concentrators as a mixture with the remaining two, the sandstone and carbonate lithological layers. Table 1 exhibits an average lithological ore composition, including Cu, Ag and C_{org} contents, which is used as a feed in the processing plants in the 90's of the previous century. In Table 2, similar data for 2004 are put together to emphasize almost double increase of the shale fraction content in the feed of the KGHM Polish Copper S.A. processing plants.

Ore component	Rudna	Polkowice – Sieroszowice	Lubin
Carbonate ore %	51.0	84.0	38.0
Shale ore, %	5.0	6.0	8.0
Sandstone ore, %	44.0	10.0	54.0
Cu content, %	2.05	1.81	1.36
Ag content, g/Mg	47	34	68
C _{org} content, %	0.64	1.14	1.76

Table 1. Composition of lithological ore layers and content of copper, silver, and organic carbon in feed of the KGHM copper concentrators in nineties (Luszczkiewicz, 2000)

Ore component	Rudna	Polkowice – Sieroszowice	Lubin
Carbonate ore %	33	75	25
Shale ore, %	11	17	15
Sandstone ore, %	56	8	60
Cu content, %	2.23	2.03	1.28
Ag content, g/Mg	53	40	67
C _{org} content, %	1.49	1.66	1.62

 Table 2. Composition of lithological ore layers and content of copper, silver, and organic carbon in feed of the KGHM copper concentrators in 2004 (Luszczkiewicz 2004)

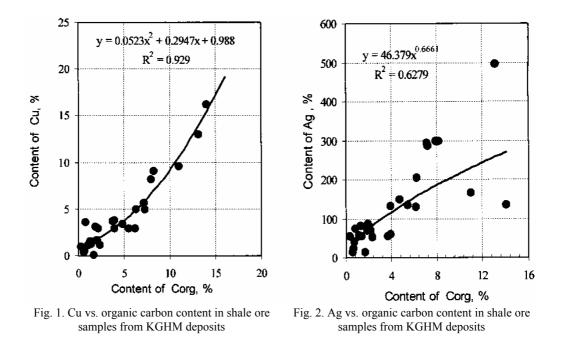
A remarkable increase of the black shale content in the mined (up to 27 % for Lubin) ore is currently observed (Kubacz and Skorupska, 2007). In Table 3, results of investigations of samples of the ore taken from one of the mining areas of ZG Lubin in 2004 (Luszczkiewicz 2004) are put together. As it can be seen in the table, when the volumetric distribution of the shale in the ore is 15%, the distribution of copper and silver originating in this shale in the working face is over 45%. For C_{org} , this distribution is about 80%. The C_{org} content in the ore is strictly related to the shale fraction content. C_{org} in the ore mainly originates from the shale fraction, therefore, under particular conditions of upgrading, the product enriched in this component will be of similar character to the shale fraction.

 Table 3. Lithological composition and distribution of copper and organic carbon of working face in the Lubin Mine (region G1, Malomice I) (Luszczkiewicz 2004)

Name of the sample	Layers of	Volume- tric	Cu	, %	Ag, g	g/Mg	C _{org} , %	
	the thickness m	distribution	Content	distribu- tion	Content	distribu- tion, %	Content	distribu- tion
Dolomitic-clay shale	0.10	5.32	2.96	10.09	134	8.77	6.40	26.05
Clay shale	0.18	9.57	5.74	35.21	293	34.51	7.19	52.67
Boundary dolomite	0.10	5.32	0.75	2.56	42	2.75	0.73	2.97
Grey sandstone	1.50	79.79	1.02	52.14	55	53.98	0.30	18.31
Mixed ore (calculated)	1.88	100.00	1.56	100.00	81	100.00	1.31	100.00
Mixture assay			1.64		83		1.36	

Chemical analysis of the ore samples and lithological layers taken from different mining areas of the KGHM Polish Copper S.A. proved a clear correlation between C_{org} content and metal concentration. The correlation metal content vs. C_{org} content for copper and silver are shown in Figures 1 and 2.

According to claim of technologists, the shale fractions presence in the feed for flotation causes severe difficulties in the technological processes of the mixed ores. The flowsheets became very complex and unit operations very expensive, even though technological systems have recently been modernized. The growing distribution of difficult-to-upgrade shale fraction is also a major reason for the metal losses in the flotation tailings (Luszczkiewicz, 2000).



During crushing considerable difficulties with liberation of sulphide minerals from the shale layer take place. Simultaneously, a part of clay and organic components, which are easily liberated from the shale, can make the flotation of copper sulphide minerals difficult. The easy-flotating fines of clay minerals liberated during grinding and impregnated with organic matter create slime coating on the air bubbles and sulphide minerals hindering flotation. Undoubtedly, apart from very fine granulation of sulphide minerals in the shale, it is one the most important reasons of difficulties in the flotation process of the feed containing the shale lithological layer.

THE CONCEPT AND AIM OF INVESTIGATION

The aim of the investigation considered in this work was to test the effect of nonoxidative leaching of the by-product (middlings) from the first cleaning operation of the Lubin Concentrator (ZWR Lubin) on flotation effectiveness. The tailing from the 1st cleaning flotation operation at this plant is recognized as the most troublesome product in the existing flotation circuit at the Lubin Concentrator due to a high amount of the difficult-to-treat shale fraction. It was the main reason of choosing it as the material for investigations. Under technological condition at the Lubin Concentrator, this product represents 20-30% of the mass of solids circulating in the whole flotation system, with copper recovery of about 20-25%.

Non-oxidative leaching of shale fraction is a part of the concept to change the technology, which has been developed by the Wroclaw University of Technology in the frame of the European Union BIOSHALE project. The concept scheme was shown

in Fig. 3 (BIOSHALE, Deliverable D.4.2, 2006; Chmielewski and Charewicz, 2006). According to the general concept of the project, the difficult-to-upgrade shale fraction should be separated from the existing flotation circuits and applied for further, individual, bio- or hydrometallurgical processing. Using non-oxidative leaching with sulphuric acid solutions is the only chance for successful liberation of the minerals disseminated in the shale carbonate and organic matter as well as for enhance the flotation efficiency.

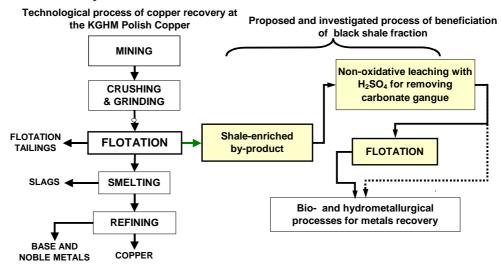


Fig. 3. General BIOSHALE concept of separate processing of black shale ore fraction from Polish copper deposits

EXPERIMENTAL

MATERIALS AND METHODS

Non-oxidative leaching

Non-oxidative leaching of the shale fraction of the copper ore or its processing byproducts from the KGHM technological circuits was used as a unit operation which aim was to liberate metal-bearing minerals from carbonate particles. This kind of leaching consists of selective (without breaking sulphides) chemical calcium and magnesium carbonates decomposition by means of sulphuric acid, according to the reactions:

$$CaCO_3 + H_2SO_4 + H_2O = CaSO_4 \cdot 2H_2O \downarrow + CO_2 \uparrow$$
(1)

$$MgCO_3 + H_2SO_4 = MgSO_4 + CO_2\uparrow + H_2O$$
(2)

Hydrated calcium sulfate (gypsum) precipitates as a solid reaction product, whereas water-soluble magnesium sulfate and gaseous carbon dioxide are other reaction products. Since particles of middlings are fine, leaching of the carbonate gangue with H_2SO_4 is very rapid and can be performed at ambient temperatures in reactors with mechanical stirring of a simple construction.

The amount of H_2SO_4 applied in the non-oxidative leaching operation directly corresponds to the content of carbonates and must be precisely controlled to maintain the final pH of the pulp at a level enabling its direct transfer either to the flotation circuit without a need for pH correction or to the leaching and bioleaching. Therefore, for further flotation, the amount of sulfuric acid introduced to the leaching operation should always be kept below the analytically determined maximum amount of acid required for the total carbonates decomposition.

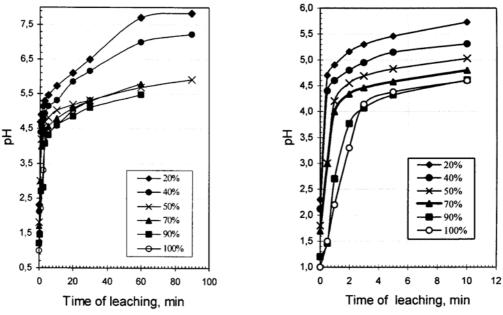


Fig. 4. pH vs. leaching time plots for nonoxidative leaching of Lubin middlings

Fig. 5. pH vs. leaching time plots for initial stage of non-oxidative leaching of Lubin middlings

Kinetics of non-oxidative leaching of the middlings from the Lubin Concentrator was investigated for different degrees of carbonates decomposition varying from 20 to 100 %. The key parameter determining the amount of H_2SO_4 required for carbonates leaching is the maximum demand for acid ($z_{H_2SO_4}^{max}$), which is the mass of pure H_2SO_4 necessary for a total decomposition of carbonates in 1 kg of dry solid feed. The $z_{H_2SO_4}^{max}$ parameter should be determined analytically from laboratory tests. H_2SO_4 is introduced to the reactor containing shale slurry at a rate that assures its total

utilization. The maximum demand for sulphuric acid for examined Lubin middlings was $494 \text{ g H}_2\text{SO}_4/\text{kg}$ of dry material.

The process control of non-oxidative leaching is based on pH measurement of leached middlings suspension after introduction of desired amount of sulphuric acid. On the basis of kinetic results for Lubin middlings it was found that the process is very rapid (Figs. 4 and 5) and after about 5 minutes almost entire amount of acid is already used up. The observed further pH changes (up to about 40-60 minutes) correspond to the saturation of the slurry with CO_2 .

Non-oxidative leaching is not only very fast but also selective. It does not cause chemical decomposition of metal sulphides under non-oxidative conditions created by the carbon dioxide.

The samples of middlings being the tailings from the 1st cleaning operation at the Lubin Concentrator before and after non-oxidative leaching with sulfuric acid were the material for experiments. The total time of carbonate decomposition in the examined samples was 60 minutes.

Flotation feeds with either 50, 70 or 90 % of carbonate decomposition were used in experiments performed according to the flow-sheet shown in Fig. 6. For comparison, the flotation of raw middling (i.e. non-leached with H_2SO_4) was also carried out. For the flotation experiments a Mekhanobr sub-aeration type laboratory flotation machine equipped with a 1dm³ cell was applied. pH measured during the flotation for the non-leached material was from 7.6 to 8.3, and for the leached samples from 5.5 to 7.0.

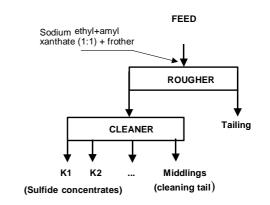


Fig. 6. Flotation experiments

In the standard xanthate flotation of sulfides, 50-60g/Mg of collector (mixture of sodium ethyl+amyl xanthate, 1:1) and 10-20g/Mg of frother (Corflot) were used. The rougher flotation was conducted up to the moment when the flotation froth did not contain useful minerals. The obtained concentrate was subsequently subjected to the cleaning flotation where the following products of flotation were collected at suitable time intervals. The procedures of the flotation experiments were the same, but quantities of the reagents and times intervals of the products collection were different for various examined feed.

Because of the strong frothing properties of the suspension after leaching, experiments were carried out with a minimal air-flow. This caused low yield of the products and resulted in higher selectivity of flotation.

RESULTS AND DISCUSSION

PARTICLE SIZE DISTRIBUTION

(i)	Materia	l non-lea	ched – 0%	6 of carbo	nate decc	mpositio	n		
(ii) Particle size,	Yield	Cu	, %	Ag, g	g/Mg	Corg	,%		
μm	γ, %	λ	E	λ	Ę,%	λ	E		
>100	6.94	4.20	12.87	268	13.69	8.80	7.43		
71 - 100	8.93	3.16	12.45	197	12.93	12.50	13.56		
40 - 71	34.13	2.45	36.89	131	32.88	10.30	42.72		
25 - 40	17.46	1.83	14.10	103	13.22	6.35	13.47		
<25	32.54	1.65	23.69	114	27.28	5.77	22.82		
Feed calculated	100.00	2.27	100.00	135.99	100.00	8.23	100.00		
	50	% of carl	bonate de	compositi	on				
>100	6.57	4.42	10.85	284	11.77	10.80	7.07		
71 - 100	9.86	3.28	12.07	188	11.69	14.60	14.33		
40 - 71	32.16	2.83	33.98	156	31.65	11.60	37.15		
25 - 40	16.20	2.56	15.48	135	13.79	8.16	13.16		
<25	35.21	2.10	27.61	140	31.09	8.07	28.29		
Feed calculated	100.00	2.68	100.00	158.53	100.00	10.04	100.00		
	70	% of carl	bonate de	compositi	on				
>100	6.95	4.32	10.73	196	8.16	11.40	7.83		
71 - 100	9.93	3.28	11.64	208	12.37	15.10	14.81		
40 - 71	29.03	2.94	30.52	174	30.26	12.70	36.43		
25 - 40	14.39	2.95	15.18	157	13.54	9.28	13.20		
<25	39.70	2.25	31.94	150	35.68	7.07	27.74		
Feed calculated	100.00	2.80	100.00	166.93	100.00	10.12	100.00		
	90	% of carl	bonate de	compositi	on				
>100	5.69	4.46	8.31	296	9.00	11.90	6.21		
71 - 100	11.11	3.39	12.34	204	12.11	16.10	16.39		
40 - 71	30.08	3.14	30.93	186	29.89	13.20	36.38		
25 - 40	12.20	3.40	13.58	175	11.40	10.50	11.73		
<25	40.92	2.60	34.84	172	37.60	7.81	29.29		
Feed calculated	100.00	3.05	100.00	187.19	100.00	10.91	100.00		

 Table 4. Particle size distribution of tailing from the 1st cleaning flotation operation at the Lubin Concentrator

 $\gamma\,$ - yield of fraction in product, $\%\,$

 λ - content of component in fraction, %

 ε - recovery of component in fraction, %

Table 4 shows the particle size distribution of the examined raw middlings and samples after non-oxidative leaching. For respective size fractions the contents (λ) of copper, silver, and organic carbon and their distribution (ϵ) are mentioned. It can be seen that the size fraction <40 µm contains 50% of the non-leaching middlings (raw by-product) mass. For the leached materials the content of this fraction increases only several per cent (2-4%).

Therefore, we can say that leaching slightly influences grinding of the material. It is observed that with the increase of carbonates leaching in the investigated sample, there is an increase in useful liberated components in the fractions. The biggest recovery of Cu, Ag and C_{org} was observed in the 0-25 μ m and 40-71 μ m size fractions, whereas the recovery of the liberated Cu and Ag components of the <25 μ m size fraction grows with the increase of carbonates distribution in the sample.

Copper distribution vs. particle size plot for the Lubin middlings is shown in Fig. 7, whereas distribution of Cu, Ag and C_{org} for feed after 70% of carbonate decomposition are given in Fig 8.

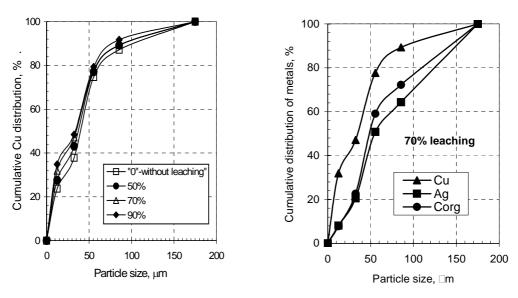


Fig. 7. Copper distribution vs. particle size of Lubin middlings for various carbonates leaching degree

Fig. 8. Cu, Ag and organic carbon distribution vs. particle size of Lubin middlings

The contents of Cu, Ag and C_{org} for the examined middlings feeds after different carbonates leaching degree are shown in Table 5. It is well seen that even partial carbonates leaching with sulphuric acid causes remarkable metal-bearing minerals liberation from carbonates intergrowths. It is revealed by an increase in metal contents in the examined samples.

% of carbonate decomposition	Cu, %	Ag, ppm	Pb %	C _{org} %	Co, ppm	Ni, ppm	Zn, %	Fe, %
0%	2.27	136	1.27	8.23	505	322	0.114	1.474
50%	2.68	159	1.49	10.04	513	335	0.106	1.459
70%	2.80	167	1.59	10.12	530	348	0.124	1.422
90%	3.05	187	1.83	10.91	564	356	0.111	1.366

 Table 5. Change of metals and organic carbon content in flotation feed after non-oxidative leaching of various carbonates decomposition degree

RESULTS OF FLOTATION EXPERIMENTS

Table 6 shows the results of flotation experiments with middlings when sodium ethyl+amyl (1:1) xanthate was used as the collector. Flotation of the non-leached material was conducted for comparison with all experiments of this series of tests. The upgrading plots are presented in Figures 9 to 10. They contain the relationship between recovery of valuable components versus their content in the concentrate. It can be seen from Fig. 9 that the increase of the carbonates decomposition degree leads to a remarkably better upgrading of Cu, Ag and C_{org}. It is particularly important for recovery exceeding 80 %.

Figure 10 presents a relationships between recovery of valuable components in concentrate (Cu, Ag, C_{org}) and recovery of a second component (of barren part of the ore) in the tailings. This method of graphical interpretation of upgrading data is referred as the Fuerstenau upgrading curve (Drzymala and Ahmed, 2005). This type of upgrading curve enables to compare enrichment of different components of various ores having different feed composition in one graph. In the plot shown in Fig.10 one can well see an upgrading increase of the examined components taking place with increasing the leaching degree of the carbonates.

	Material non-leaching – 0% of carbonate decomposition										
	Yield	Cu			Ag				C _{org}		
Product	. %	, %	β, %	ę,%	, g/Mg	β, g/Mg	ε, %	, %	β, %	ε, %	
C1	2.64	5.23	5.23	6.02	283	283.00	5.38	10.35	10.35	3.42	
C2	14.15	4.22	4.38	26.06	241	247.60	24.58	10.42	10.41	18.47	
C3	12.18	3.09	3.84	16.43	190	223.39	16.68	11.04	10.67	16.84	
Cleaning tail	43.26	2.15	2.83	40.58	134	169.86	41.76	8.96	9.65	48.54	
Tailing	27.77	0.90	2.29	10.90	58	138.80	11.60	3.66	7.99	12.73	
Feed calculated	100.00	2.29		100.00	138.80		100.00	7.99		100.00	
Feed assay		2.32			132			8.25			
	50% of carbonate decomposition										
			cont	inuation:	see next	page					

Table 6. Results of standard xanthate flotation of middlings. Mixture of sodium ethyl+amyl xanthate (1:1) 50-60g/Mg, frother (Corflot) 10-20g/Mg

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			continu	ation from	m previo	us page				
	Ν	laterial n	on-leach	ing – 0%	of carbo	nate deco	mpositio	n		
	Yield		Cu			Ag			Corg	
Product	%	λ, %	β, %	Ę,%	λ, g/Mg	β, g/Mg	ε, %	λ, %	β, %	ε, %
C1	3.42	4.34	4.34	6.38	249	249.00	5.87	13.27	13.27	5.21
C2	14.77	3.82	3.92	24.24	223	227.89	22.71	12.83	12.91	21.74
C3	49.84	2.82	3.11	60.39	177	190.61	60.83	11.59	11.94	66.28
Cleaning tail	5.99	1.24	2.96	3.19	96	182.95	3.97	3.57	11.27	2.45
Tailing	25.98	0.52	2.33	5.80	37	145.03	6.63	1.45	8.72	4.32
Feed calculated	100.00	2.33		100.00	145.03		100.00	8.72		100.00
Feed assay		2.34			138			8.40		
			70% of	carbonat	e decom	oosition				
C1	7.75	4.44	4.44	14.25	248	248.00	12.50	13.73	13.73	11.68
C2	16.27	3.88	4.06	26.15	234	238.52	24.76	13.57	13.62	24.25
C3	42.32	2.94	3.35	51.54	188	206.29	51.74	12.47	12.89	57.96
Cleaning tail	8.93	1.18	3.09	4.36	101	193.80	5.86	4.02	11.84	3.94
Tailing	24.72	0.36	2.41	3.69	32	153.80	5.14	0.80	9.11	2.17
Feed calculated	100.00	2.41		100.00	153.80		100.00	9.11		100.00
Feed assay		2.25			141			8.23		
			90% of	carbonat	e decom	oosition				
C1	8.77	4.83	4.83	18.01	393	393.00	17.41	13.71	13.71	13.73
C2	36.31	3.46	3.73	53.45	208	224.42	51.26	14.10	14.02	58.42
C3	19.75	2.74	3.43	23.03	176	209.67	23.60	10.92	13.08	24.62
Cleaning tail	10.02	0.74	3.07	3.15	71	191.11	4.83	1.7	11.56	1.94
Tailing	25.15	0.22	2.35	2.35	17	147.32	2.90	0.45	8.76	1.29
Feed calculated	100.00	2.35		100.00	147.32		100.00	8.76		100.00
Feed assay		2.31			142			8.54		

Comparing the feeds of different carbonate decomposition degree it can be concluded, that flotation of the feed after 90 % of carbonates decomposition leads to high grade concentrates and the lowest losses of the examined components in tailings. This is the consequence of the best material upgrading. It should be pointed out, that even the feed after 50 % of carbonates decomposition can be characterised by evidently better selectivity of the flotation in comparison with the non-leached feed.

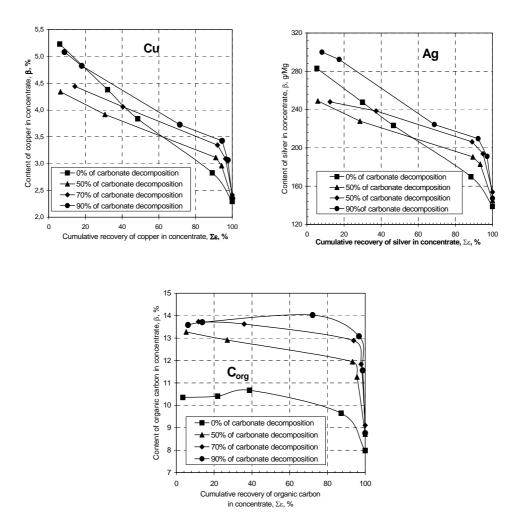


Fig. 9. Recovery – Cu, Ag, C_{org} content upgrading curves of xanthate flotation of middlings of different carbonates distribution degree (50%, 70% and 90%). Based on data from Table 6

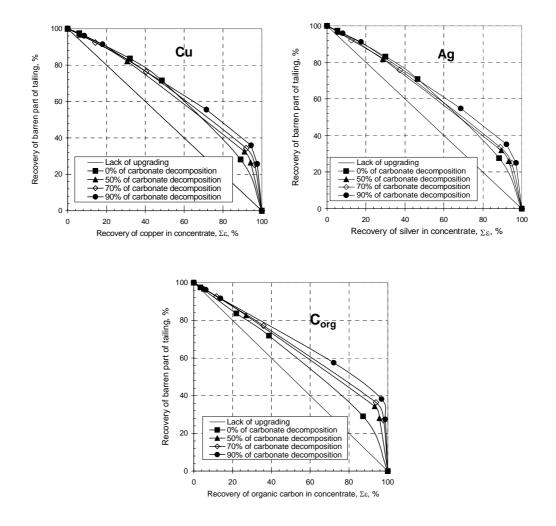


Fig. 10. Comparison of xanthate flotation of 1st ZWR Lubin cleaning middlings for different carbonates leaching degrees for Cu, Ag and C_{org} recovery in concentrate vs. barren part of tailing. Based on data from Table 6

CONCLUSIONS

1. Investigated middlings, being the tailing from the 1st cleaning flotation operation at the Lubin Concentrator is recognized as the most troublesome product in the existing flotation circuit due to a high amount of the difficult-to-treat shale fraction. Fine dissemination of sulfide minerals is the main reason of difficulties in upgrading of the shale fraction. It was the major reason for choosing the middlings as the material for the presented investigations

- Flotation experiments proved that upgrading the middlings was nearly impossible. Material containing about 2% Cu and 8% of organic carbon provided concentrates containing 3-4% Cu and 8-10% of organic carbon
- 3. Non-oxidative leaching of Lubin middlings with H_2SO_4 can be used as an effective operation for selective chemical liberation of sulphide minerals before flotation
- 4. Partial decomposition of carbonates from 50 to 90% remarkably improves the liberation degree of the useful minerals from the hydrophilic intergrowths with carbonate matter
- 5. Evidently improved flotation of Cu, Ag and C_{org} occurs for leached materials in comparison with direct flotation of untreated raw materials
- 6. An increase of the carbonates decomposition of the feed results in enhanced recovery and content of the useful components in the concentrate
- 7. The best results of the flotation parameters (recovery and concentrate grade) were obtained for the feed with the 90 % of carbonate decomposition.

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Opisano mineralogiczno-petrograficzne właściwości czarnych łupków obecnych w złożu rud miedzi Monokliny Przedsudeckiej. Omówiono specyfikę zachowania się warstwy łupkowej w stosowanym procesie technologicznym przeróbki rud. Przedstawiono koncepcję pozyskiwania części frakcji czarnych łupków z urobku kierowanego do zakładu przeróbczego ZWR Lubin poprzez wydzielenie produktu pośredniego stanowiącego odpad operacji pierwszego czyszczenia koncentratu. Stwierdzono, że badany produkt pośredni jest materiałem praktycznie niewzbogacalnym, odznaczającym się podwyższoną zawartością węgla organicznego podobną do zawartości w petrograficznie "czystych" czarnych łupkach. Uznano, że produkt ten może być uważany za gotowy koncentrat łupkowy do procesów bio- i hydrometalurgicznych. Przedstawiono wyniki ługowania nieutleniającego H₂SO₄ opisanego półproduktu. Stwierdzono, że ługowanie nieutleniające jest procesem selektywnym, w którym chemicznemu rozkładowi węglanów wapnia i magnezu towarzyszy uwolnienie siarczkowych minerałów użytecznych. Częściowe wyługowanie węglanów (między 70 a 90% całkowitej zawartości węglanów) za pomocą kwasu siarkowego w istotny sposób poprawia stopień uwolnienia minerałów użytecznych. Przejawia się to wzrostem uzysku i zawartości wszystkich metali zawartych w koncentratach flotowanych z półproduktu łupkowego poddanego ługowaniu nieutleniającemu