Possibilities of Obtaining Metals from Polymetallic Ore from Zlate Hory

Věra VRLÍKOVÁ[1], Vladimír ČABLÍK[2], Iva JANÁKOVÁ[3]

[1] VŠB – Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu 15, 708 33 Ostrava – Poruba, Czech Republic; email: vera.vrlikova@vsb.cz
[2] VŠB – Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu 15, 708 33 Ostrava – Poruba, Czech Republic; email: vladimir.cablik@vsb.cz
[3] VŠB – Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu 15, 708 33 Ostrava – Poruba, Czech Republic; email: iva.janakova@vsb.cz

http://doi.org/10.29227/IM-2019-02-05

Submission date: *21-08-2019* | Review date: *12-10-2019*

Abstract

The study deals with the use of flotation to obtain metals from the polymetallic ore from Zlate Hory, the Czech Republic. X-ray diffraction was performed, on the basis of which the mineralogical composition was determined in the sample. The most abundant was quartz with 87.03%. From ore minerals were detected pyrite 2.30%, sphalerite 3.64% and chalcopyrite 1.59%. Due to the high quartz content in the sample, heavy medium separation was selected to reduce its content. The treated polymetallic ore sample was subjected to flotation. In the flotation, the reagents xanthate was used as a collector, and pine oil as a frother. Different flotation conditions were observed, based on which the most suitable conditions for the flotation of metals were determined.

Keywords: chalcopyrite, copper, flotation, metals, polymetalic ores, Zlate hory

Introduction

In the processing of raw materials new treatment methods optimization and innovation are used with regard to environmental protection (Jakabský et. Al., 1997). Flotation is used, among other industries, in the processing of mineral resources, where valuable minerals are obtained from ores (Liu et al., 2018). It is a method of physico-chemical separation utilizing different mineral surface properties. It uses the hydrophobic character of minerals able to bind to air bubbles. Mineral air bubbles rise through the mash and concentrate as froth (Yin et al., 2017). Among some factors, the flotation performance may depend on the mineralogical composition of the processed ore, the performance of the flotation cells, the aeration, the hydrodynamic conditions of the pulp, the grain size distribution or the mineral release from the ore after grinding (Liu et al., 2018). The fastest flotation and maximum recovery of metals are associated with the mean particle size. For fine-grained particles, the degree of release is maximal, so recovery from flotation depends on other factors, but in coarse particles obviously it depends on the degree of release (Markovic et. Al., 2008). The type and dose of the agent also have a strong effect on flotation behaviour and should be carefully analyzed to increase the recovery of valuable components. One of the main conditions is the efficient use of reagents that minimize operating costs (Sousa et al., 2017).

Natural copper is rare and represents about 1% of all copper compounds. Copper may be present either in the form of sulphide ores, forming 90% of copper compounds, or 9% as oxidic ores (Pietrzyk, Tora, 2018). Chalcopyrite is one of the most important minerals in copper. The quality of the raw material is reduced by the presence of sulphide minerals (e.g. pyrite or sphalerite) and non-sulphide minerals (e.g. quartz) (Owusu et al., 2014). The present pyrite reduces the quality of the copper concentrate, thereby increasing the economic cost of processing. The released copper from chalcopyrite activates pyrite, causing its problems in the transition to froth. One possible method of suppressing its flotability is to increase the pulp pH, thereby increasing lime consumption (Zhong et al., 2015). Chalcopyrite, without any impurities present in the crystal structure, is a stable mineral and does not oxidize readily. It is believed that chalcopyrite oxidizes in an acidic environment where it appears as H+, Cu2+, Fe2+ and SO in solution (Bulatovic, 2007). In froth flotation, the most commonly used collectors for the separation of sulphide minerals are copper xanthates. Chalcopyrite floats quite well in a small amount of xanthate over a wide pH range (Kalegowda et al., 2015).

Zlate Hory (ZH) is one of the most important deposits in the eastern edge of the Bohemian Massif (Novotný and Zimák, 2003). The gold-mining ore district is an area of about 25 km2 near the town of Zlate Hory. It is an interesting locality for primary deposits ZH-South and ZH-Mining rocks, which are typical for the occurrence of monometallic Cu mineralization. ZH-East is a typical site in which Cu-Pb-Zn-Ag mineralization occurs and in addition to Au in the ZH-West region. Mining was terminated here on December 31, 1993 (Grygárek, 2006). Zlate Hory-East is located in the eastern and south-eastern Zlate Hory ore district, which forms part of the Vrbno Formation. The deposit is formed by chalcopyrite, pyrite, sphalerite and galenite. Copper deposits are found in the surface layers, whereas zinc and lead deposits are found deeper. Cu mineralization is 0.3–0.55% Cu and 1.0% for Pb-Zn (Kafka, 2003).

Tab. 1. X-ray diffraction results
Tab. 1. Wyniki analizy RTG

mineral	quartz	pyrite	**chalcopyrite**	sphalerite	albite	chlorite	muscovite	barite
content [%]	87.03	2.30	**1.59**	3.64	1.89	1.28	0.48	1.59

Tab. 2. X-ray fluorescence spectrometry results ore sample
Tab. 2. Rentgenowska spektrometria fluorescencyjna – wyniki analizy

element	Al	Si	S	Cr	Mn	Fe	**Cu**	Zn	As	Cd	Ba	Pb	LE*
content [%]	0.65	19.30	2.91	0.18	0.03	2.28	**0.50**	1.83	0.01	0.01	0.85	0.08	71.35

* LE (light elements)

Tab. 3. X-ray diffraction results
Tab. 3. Wyniki analizy RTG

mineral	quartz	pyrite	**chalcopyrite**	sphalerite	albite	chlorite	barite
content [%]	68.13	10.13	**2.59**	12.85	1.99	2.38	1.93

Tab. 4. X-ray fluorescence spectrometry results ore sample
Tab. 4. Rentgenowska spektrometria fluorescencyjna – wyniki analizy

element	Al	Si	S	Cr	Mn	Fe	**Cu**	Zn	As	Cd	Ba	Pb	LE*
content [%]	0.78	22.90	5.98	0.22	0.07	5.75	**1.14**	6.46	0.04	0,01	0.71	0.18	56.77

Materials and methods

For this work, a sample of polymetallic ore was used from Zlate Hory-East. For laboratory tests, it was necessary to adjust the sample by crushing and grinding, followed by sorting to a grain size of -200 μm. Granulometric analysis of the treated sample showed that most of the sample are represented by a grain size of 30–60 μm.

This modified sample was subjected to X-ray diffraction to determine the mineral content (Tab. 1). A substantial part of the polymetallic ore production was represented by quartz (87.03%). Other non-metallic minerals represented were barite, albite, chlorite and muscovite. The abundance of pyrite, chalcopyrite and sphalerite was determined from ore minerals. The largest amount in the sample was sphalerite 3.64%. Chalcopyrite amounted to 1.59%.

Elemental composition was determined using X-ray fluorescence analysis (Tab. 2). X-ray fluorescence spectrometry revealed the largest content of light elements (LE) 71.35%. Of the main ore minerals, Fe content was 2.28%, Zn 1.83% and Cu 0.50%. In addition to the aforementioned elements in the table, other elements in trace amounts occurred in the polymetallic ore.

To reduce the quartz content of the sample we used heavy medium separation. The medium was bromoform 98.8% with a density of 2.828 $g.cm^{-3}$. The sample was treated for 3 days, when mixed three times a day. The sample was washed with methanol and distilled water, and let to dry at 105°C.

The obtained sink fraction was subjected to flotation tests. Flotation tests were performed on a pneumatic-mechanical flotation machine VRF-1 with a flotation cell volume of $1dm^3$. Sodium ethylxanthate (SEX) was used as the collector, the pine oil was the frother and $CaOH_2$ was used to adjust the pH. The flotation scheme is shown in Figure 1. For each experiment we used 30 g of sample. The sample was stirred for 2 minutes after adjusting the pH. Subsequently, the collector was added and stirring continued for 2 minutes, the frother was added and stirred for 1 minute. Two concentrates were obtained after 5 and 10 minutes.

Results and discussion

Heavy medium separation:

For subsequent flotation tests, a sink fraction was used, which contained primarily sulphide minerals. A substantial part was formed by floating fractions containing mainly quartz and non-sulphide minerals.

The sink fraction was subjected to X-ray diffraction (Tab. 3) and X-ray fluorescence analysis (Tab. 4). Based on X-ray diffraction, the content of quartz was reduced to 68.13% from 87.03%. The content of sulphide ores increased, in the case of sphalerite to 12.85%, pyrite to 10.13% and chalcopyrite to 2.59%.

X-ray fluorescence analysis determined the contents of individual metals in the sample. After heavy medium separation, the content of the individual elements increased. Copper increased from 0.50% to 1.14%.

Heavy medium separation resulted in an increase in the mineral content, but there was no complete removal of quartz.

Flotation:

The first flotation focused on selecting the most suitable flotation agent ratio. Tab. 5 shows an overview of the individual amounts of flotation agents used for flotation. With each additional flotation there were greater amounts of flotation reagents.

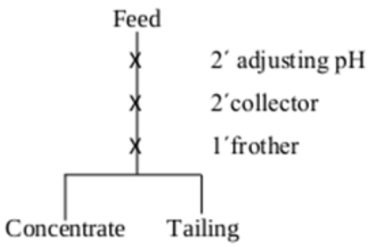

Fig. 1. Flotation scheme
Rys. 1. Schemat flotacji

Tab. 5. Overview of flotation agents for single flotation
Tab. 5. Przegląd środków flotacyjnych do pojedynczej flotacji

pH	content Cu [%]	enrichment Cu [%]
8	2.58	2.27
9	2.25	1.98
10	1.77	1.56
11	2.21	2.03

Tab. 6. Content of Cu and enrichment of CU in the sample
Tab. 6. Zawartość Cu i wzbogacenie Cu w próbce

	content Cu [%]	enrichment Cu [%]
1. flotation	1.63	1.43
2. flotation	2.23	1.96
3. flotation	2.27	2.00
4. flotation	2.47	2.17

Figure 2 and Table 6 show the results of flotation tests. From the result of the flotation it is evident that in the first flotation (21 g/t SEX and 1293 g/t pine oil) the highest yield was in Cu 87,27%, but on the contrary the lowest Cu content 1.63% and also the lowest Cu enrichment of 1.43%. The second flotation (31.5 g/t SEX and 1940 g/t pine oil) had a Cu yield of 80.00% with content Cu 2.23% and with 1.96% enrichment of Cu. The highest content Cu was achieved in the fourth flotation (52.50 g/t SEX and 3233 g/t pine oil), which was 2.47% and also the highest enrichment Cu 2.17%. Although there was the highest content Cu and enrichment Cu, there was the lowest Cu yield of 78.75%. The efficiency of the individual flotations increased with the amount of flotation agents added. According to the results, a fourth flotation was selected for further flotation tests, using 52.50 g/t SEX and 3233 g/t pine oil.

The aim of the second part of the flotation tests was to select the optimal pH at which pyrite was suppressed. For the suppression of pyrite, an alkaline medium with a pH of 8, 9, 10 and 11 was selected.

Figure 3 and Table 7 show the results of flotation tests for a single pH. At pH 11, the highest Cu yield was found to be 83.35% with content Cu 2.21% in the concentrate. The enrichment Cu in this flotation was 2.03%. The lowest Cu yield was obtained at pH 9 43.76% with content Cu 2.25%. In contrast, at pH 10 was the lowest enrichment Cu 1.56%. Based on these results, it is possible to conclude that pH 11 is best in obtaining Cu. At the same time, the flotation efficiency increases with increasing pH. At pH 11, the efficiency was 43.76%, while the pH 9 was only 22.37%.

Figure 4 shows the results of pyrite suppression at individual pH values. As the pH increased, the pyrite content of the concentrates was reduced. At pH 8 the pyrite content was 31.75%, but at pH 11 the pyrite content was only 6.42%. Together with increasing pH, the content of chalcopyrite in the sample at pH 11 was reduced to 3.67%.

Conclusion

A sample of polymetallic ores from the Zlate Hory-East deposit was subjected to flotation. The sample was adjusted to a suitable grain size and subjected to X-ray and XRF analysis. On the basis of the obtained results, the separation of quartz in heavy medium separation and subsequent flotation was performed.

First, the effect of the amount of flotation agent on the flotation efficiency was observed, which increased with a higher dose. The second series of flotation was used to determine pH at which to achieve maximum suppression of pyrite. Based on the result, we aimed to suppress pyrite and thereby increase the Cu content in the concentrate in the optimum pH 11. With increasing pH also flotation efficiency increased.

In the original polymetallic ore, the Cu content was 0.50% after subsequent treatment and flotation tests, the Cu content was increased to 2.27%.

Acknowledgments

This work was supported by Student Grant Project SV5119971 Waste from mining activities – raw material resources, Project sustainability reg. No. LO1406 - Insti-

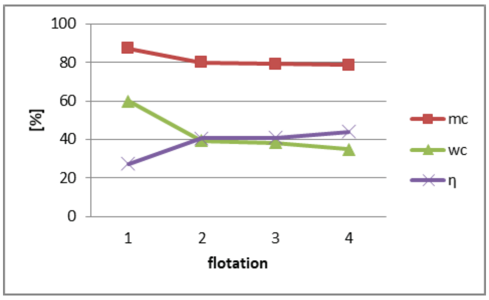

Fig. 2. Results of flotation tests [mc – metal yield to concentrate, wc - yield of the tailing the to waste, η – efficiency]
Rys. 2. Wyniki badań flotacyjnych [mc – wychód metalu, wc – wychód odpadów , η – wydajność]

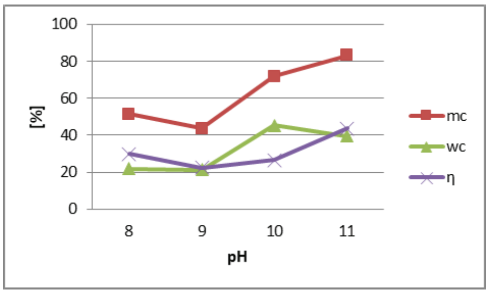

Fig. 3. Results of flotation tests [mc – metal yield to concentrate, wc – yield of the tailing the to waste, η – efficiency]
Rys. 3. Wyniki badań flotacyjnych [mc – wydajność koncentracji metalu, wc – wydajność odpadów, η – wydajność]

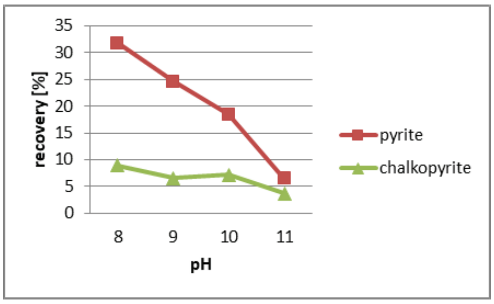

Fig. 4. Results of recovery pyrite and chalcopyrite
Rys. 4. Wyniki uzysku pirytu i chalkopirytu

Tab. 7. Content of Cu and enrichment of CU in the sample
Tab. 7. Zawartość Cu i stopień wzbogacenia Cu w próbce

	SEX [g/t]	Pine oil [g/t]
1. flotation	21	1293
2. flotation	31.50	1940
3. flotation	42	2587
4. flotation	52.50	3233

tute of Clean Technologies for Mining and Use of Energy Raw Materials and the grant program "Support for Science and Research in the Moravian-Silesian Region 2018" (RRC/10/2018) and financed from the budget of the Moravian-Silesian Region.

Literatura – References

1. BULATOVIC, Srdjan M. Handbook of flotation reagents: chemistry, theory and practice. [Volume 1], Flotation of sulfide ores. Amsterdam: Elsevier, 2007. ISBN 978-0-444-53029-5.
2. GRYGÁREK, Jiří. Za hornictvím zlatohorského rudného revíru. 1. Ostrava: Klub přátel hornického muzea OKD Ostrava-Petřkovice, 2006. Hornictví včera, dnes a zítra. ISBN 80-239-7136-0.
3. JAKABSKÝ, Štefan, Michal LOVÁS, Slavomír HREDZÁK a Annamária MOCKOVČIAKOVÁ. Overview of realized research on physical processing methods of primary and secondary materials. Acta Montanistica Slovaca. 1997, 2(3), 216-218. ISSN 1335-1788.
4. KAFKA, Jan, ed. Rudné a uranové hornictví České republiky. Ostrava: Anagram, 2003. ISBN 80-863-3167-9.
5. KALEGOWDA, Yogesh, Yuet-Loy CHAN, Der-Hsin WEI and Sarah L. HARMER. X-PEEM, XPS and ToF-SIMS characterisation of xanthate induced chalcopyrite flotation: Effect of pulp potential. Surface Science. 2015, 635, 70-77. DOI: 10.1016/j.susc.2014.12.012. ISSN 00396028. Dostupné také z: https://linkinghub.elsevier.com/retrieve/pii/S0039602814003926
6. LIU, J., Han LONG, K.C. CORIN and C.T. O'CONNOR. A study of the effect of grinding environment on the flotation of two copper sulphide ores. Minerals Engineering. 2018, 122, 339-345. DOI: 10.1016/j.mineng.2018.03.031. ISSN 08926875. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0892687518301389
7. MARKOVIC, Zoran S., Aleksandar JANKOVIC a Rudolf TOMANEC. Effect of particle size and liberation on flotation of a low grade porphyry copper ore. Journal of Mining and Metallurgy. 2008, 44(1), 24-30. ISSN 1450-5959.
8. NOVOTNÝ, Pavel and Jiří ZIMÁK. Zlaté Hory: historie a současnost ložiska zlata evropského významu. 1. Olomouc: Memoria, 2003. ISBN 80-858-0720-3
9. OWUSU, Clement, Susana BRITO E ABREU, William SKINNER, Jonas ADDAI-MENSAH and Massimiliano ZANIN. The influence of pyrite content on the flotation of chalcopyrite/pyrite mixtures. Minerals Engineering. 2014, 55, 87-95. DOI: 10.1016/j.mineng.2013.09.018. ISSN 08926875. Dostupné také z: https://linkinghub.elsevier.com/retrieve/pii/S0892687513002914
10. PIETRZYK, S. a B. TORA. Trends in global copper mining – a review. IOP Conference Series: Materials Science and Engineering. 2018, 427. DOI: 10.1088/1757-899X/427/1/012002. ISSN 1757-899X. Dostupné také z: http://stacks.iop.org/1757-899X/427/i=1/a=012002?key=crossref.27835adf8a6ca30d3d7624bffbc409a2
11. SOUSA, Rui, Aurora FUTURO, Carlos Setas PIRES and Mário Machado LEITE. Froth flotation of aljustrel sulphide complex ore. Physicochemical Problems of Mineral Processing. 2017, 53(2), 758−769. DOI: 10.5277/ppmp170207. ISSN 1643-1049.
12. YIN, Zhigang, Wei SUN, Yuehua HU, Jihua ZHAI and Guan QINGJUN. Evaluation of the replacement of NaCN with depressant mixtures in the separation of copper–molybdenum sulphide ore by flotation. Separation and Purification Technology. 2017, 173, 9-16. DOI: 10.1016/j.seppur.2016.09.011. ISSN 13835866. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1383586616316689
13. ZHONG, Hong, Zhenrui HUANG, Gang ZHAO, Shuai WANG, Guangyi LIU and Zhanfang CAO. The collecting performance and interaction mechanism of sodium diisobutyl dithiophosphinate in sulfide minerals flotation. Journal of Materials Research and Technology. 2015, 4(2), 151-161. DOI: 10.1016/j.jmrt.2014.12.003. ISSN 22387854. Available from: https://linkinghub.elsevier.com/retrieve/pii/S223878541400115X

Możliwości pozyskiwania metali z rudy polimetalicznej ze złoża Zlate Hory

Badanie dotyczy wykorzystania flotacji do otrzymywania metali z rudy polimetalicznej ze złoża Zlate Hory, Republika Czeska. Przeprowadzono dyfrakcję rentgenowską, na podstawie której określono skład mineralogiczny próbki. Największą zawartość wykazał kwarc z 87,03%. Z minerałów rudnych stwierdzono piryt 2,30%, sfaleryt 3,64% i chalkopiryt 1,59%. Ze względu na wysoką zawartość kwarcu w próbce wybrano rozdział w cieczy ciężkiej w celu zmniejszenia jego zawartości. Badaną próbkę rudy polimetalicznej poddano flotacji. We flotacji zastosowano ksantantogenian jako kolektor, a olej sosnowy jako spieniacz. Zbadano różne warunki flotacji, na podstawie których określono najbardziej odpowiednie warunki flotacji metali.

Słowa kluczowe: chalkopiryt, miedź, flotacja, metale, rudy polimetaliczne, Zlate Hory