UTILIZATION OF FLOTATION IN COPPER EXTRACTION FROM POLYMETALLIC ORE

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ABSTRACT

The aim of this study was to examine flotation of utility metals from poor polymetallic ores and verify the potential for profitable yields in connection with potentially economic deposits of non-ferrous metals. The paper describes results in flotation concentrate research to recover copper from polymetallic ore. The polymetallic ore from Zlate Hory deposit (Czech Republic) was subjected to crushing, grinding, and screening to prepare feed for separation with mesh size under 200 microns. The heavy medium separation was performed in tetrabromomethane with a density of 2.967 g.cm$^{-3}$. The float and sink products were obtained and tested for chemical composition. Next, the treated polymetallic ore sample was subjected to flotation. In flotation, various dosages of collector (PAX) and various pH were tested, at which pyrite was depressed. The recovery of metallic copper in the concentrate increased with the collector dose. As the pH of the medium increased, the pyrite content in the concentrate dropped. The lowest content of pyrite, i.e. 4.01 %, was obtained at pH 10. In the original polymetallic ore, the Cu content was 0.41 % after subsequent treatment and flotation tests, the Cu content increased to 1.38 % with Cu recovery 86.18 %.

Keywords: Copper; Flotation, Polymetallic ore; Potassium amylxanthate (PAX); Zlate Hory

1 INTRODUCTION

Separation of minerals from ore is an important industrial process. Of the commonly used methods of separation, flotation exploits the hydrophobic (it is partial or incomplete wettability of a solid phase by the water) and hydrophilic (solids are completely wetted by water) properties on the mineral surface. Flotation is a method that is based on different surface properties occurring at the contact of three phases - solid (mineral particles), liquid (water), and gas (air). Hydrophobic particles adhere to air bubbles that move to the surface to form froth [1].

Sulphide ores are important sources of base metals, e.g. copper, zinc, lead. In most cases, the minerals of copper, lead, zinc and iron coexist on the deposit [2]. Selective flotation of sulphide ores presents several problems due to mineralogical properties, incomplete liberation, and chemical differences between ores [3]. Flotation is in many cases the only solution to concentrate sulphide minerals [4]. For sulphide minerals, hydrophobicity may occur due to the addition of a collector or oxidation leads to the formation of elemental sulphur, metal-deficient and sulphur-rich surface [5]. In flotation, xanthates are used as collectors in the separation of sulphide minerals. Their consumption is 300 to 500 g/t. Although there are a number of xanthates, sodium ethyl xanthate, isopropyl xanthate, sodium isobutyl xanthate or potassium amylxanthate are used in practice [6].

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 [7]. The typical contents of copper in sulphide ores is 0.6 %, particularly primary sulphides (e.g. chalcopyrite and bornite) or secondary sulphides (e.g. chalcocite and covellite) [8]. Chalcopyrite is one of the most important sulphide minerals, which is the main source of copper [9]. The presence of gangue sulphide minerals such as pyrite and non-sulphide minerals reduce the quality of concentrates [10]. It is the only naturally floatable copper mineral, for other sulphide copper minerals thiol collectors are added to create the hydrophobic surface needed for flotation [11]. Chalcopyrite floats well with moderate amounts of xanthate collectors over a wide pH range [12].

Chalcopyrite is associated with pyrite in ore; therefore, pyrite depression is required for economic recovery. The main problem of chalcopyrite and pyrite is their selectivity, which is caused by accidental activation of pyrite by dissolved Cu$^{2+}$ ions from complex sulphide ores. This increases the interaction of pyrite with collectors, thereby increasing its floatability [13]. Various agents, such as polymers, hydroxides, carbonates, cyanides, or sulphites, are used to suppress pyrite [14].
Mukunga [15] investigated the selectivity and kinetics of PAX and DANA (sodium amyl dithiophosphate) in the recovery of copper from sulphide copper-cobalt ore. Natural pH and pH 11 were observed. At natural pH, the copper content of the concentrate obtained was 16.1 % with a yield of 99.63 %. At pH 11, the copper content was 16.1 % with a yield of 99.05 %. These results showed that at natural pH and pH 11, the kinetics of copper regeneration with PAX is superior to DANA.

2 MATERIALS AND METHODS

For this work, a sample of polymetallic ore was used from Zlate Hory-East (Czech Republic). For laboratory tests, it was necessary to prepare the sample by crushing and grinding. A total of 9 kg of polymetallic ore was crushed and ground. This was followed by sizing of -200 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. Pyrite, chalcopyrite and sphalerite were present as ore minerals. The largest amount in the sample was sphalerite (3.64 %). Chalcopyrite was 1.59 %.

Table 1. X-ray diffraction results of ore sample - input

| mineral   | quartz  | pyrite | chalcopyrite | sphalerite | albite | chlorite | muscovite | barite |
|-----------|---------|--------|--------------|------------|--------|----------|-----------|-------|
| content [%]| 87.03   | 2.30   | 1.59         | 3.64       | 1.89   | 1.28     | 0.48      | 1.79  |

Elemental composition was determined using XRF analysis (Tab. 2). Of the main ore minerals, Zn content was 2.79 % and Cu 0.41 %. In addition to the elements listed in the table in polymetallic ores occurring elements in trace amounts.

Table 2. XRF analysis results of ore sample - input

| element  | Al2O3  | SiO2   | Fe2O3      | Cu    | Zn    | Pb | S |
|----------|--------|--------|------------|-------|-------|----|---|
| content [%]| 1.91   | 76.08  | 6.95       | 0.41  | 2.79  | 0.11 | 4.96 |

To reduce the quartz content of the sample, we used heavy medium separation. The modified sample was subjected to heavy medium separation. The medium was 1,1,2,2-tetrabromomethane 98.8 % with a density of 2.967 g·cm⁻³. The sample was washed with methanol and distilled water, and left to dry at 105°C.

The obtained sink fraction was subjected to flotation tests. The procedure scheme is shown in Fig. 1. Flotation tests were performed on a pneumatic-mechanical flotation machine VRF-1 with a flotation cell volume of 1dm³. For each experiment, we used 100 g/l of sample. The sample was conditioned for 2 minutes. Subsequently, the collector was added, and conditioning continued for 2 minutes, the frother was added and conditioned for 1 minute. Concentrate was obtained after 10 minutes. Potassium amylxanthate (PAX) was used as the collector, the polyethylene glycol (PEG) was the frother and Ca(OH)₂ was used to adjust the pH. It was used for flotation tests 3180 g/t PEG and 36 g/t, 42 g/t, 56 g/t, 70 g/t and 84 g/t PAX. Following the flotation tests in which the most appropriate collector dose was selected, the pH was monitored 8, 9, 10, 11.
3 RESULTS AND DISCUSSION

Heavy medium separation

A 9 kg sample of polymetallic ore was used for heavy medium separation. Of the total amount, 1 kg was obtained as a sink fraction and the remaining fraction was a float fraction. Based on XRD analysis, the float fraction was more than 90% quartz, muscovite, albite and chlorite. Because of its composition, the float fraction was not further interesting for processing.

Table 3 shows the composition of a sample of sink fraction from heavy medium separation. The application of heavy medium separation was prepared using sulphidic concentrate containing 30.10% Fe₂O₃, 11.50% Zn, 0.99% Cu, 26.88% S. The content of SiO₂ was reduced from 76.08% to 30.10%.

Table 3. XRF analysis results of sink fraction

| element | Al₂O₃ | SiO₂ | Fe₂O₃ | Cu | Zn | Pb | S |
|---------|-------|------|-------|----|----|----|---|
| content [%] | 1.35 | 30.10 | 30.10 | 0.99 | 11.50 | 0.14 | 26.88 |

Flotation

The first flotation focused on selecting the most suitable collector amount. The pH was constant during the flotation tests, the pH was 6.1. Figure 2 and Table 4 show the results of flotation tests. With increasing dose of PAX collector, Cu recovery in individual concentrates increased. The highest Cu recovery of 94.23% in the concentrate was achieved at a collector dose of 84 g/t. With increasing dose of PAX, the flotation efficiency increased. At a dose of 84 g/t PAX, an efficiency of 77.22% was achieved, while the lowest efficiency was 61.36% at a dose of 70 g/t. The highest mass recovery of 60% was obtained at the 56 g/t PAX dose, while the lowest mass recovery of 45% was at the 42 g/t PAX dose. The Cu content in the concentrates ranged from 1.12 to 1.13%, only at a dose of 36 g/t PAX the highest Cu content of 1.2% was achieved. The enrichment of Cu was in range of 1.13-1.20%. The highest enrichment of Cu was 1.20% at the dose 36 g/t and 70 g/t PAX. According to the results, a dose of 84 g/t PAX was selected for further flotation tests.
Figure 2. Results of flotation tests

$R_m$ – Cu recovery, $SE_{Cu}$ - separation efficiency of Cu, $v$ - mass recovery

Table 4. Content of Cu and enrichment of Cu in the sample

| dose collector | content Cu [%] | enrichment Cu [%] |
|----------------|---------------|-------------------|
| 36 g/t         | 1.2           | 1.20              |
| 42 g/t         | 1.13          | 1.14              |
| 56 g/t         | 1.13          | 1.14              |
| 70 g/t         | 1.19          | 1.20              |
| 84 g/t         | 1.12          | 1.13              |

Cu recovery was calculated according to the following formula [16]:

$$R_m = \frac{c(f - t)}{f(c - t)} \cdot 100\%$$

(1)

where:

$f = \text{Cu in the ore}, \ c = \text{Cu in the concentrate}, \ t = \text{Cu in tailings}, \ R_m = \text{the recovery of the valuable mineral.}$

Separation efficiency was calculated according to the formula [17]:

$$SE_{Cu} = R_m - R_g$$

(2)

where:

$SE_{Cu} = \text{separation efficiency of Cu} \ (%), \ R_m = \text{the recovery of the valuable mineral and } R_g = \text{recovery of the gangue into the concentrate.}$

Vizcarra et al. [18] studied the effect of particle shape properties on chalcopyrite flotation kinetics. The results of the study showed that the particle shape properties are only important for minerals that are characterized by slow flotation kinetics, so they are likely to be of greater importance for weakly hydrophobic particles. In the presence of PAX, the shape properties were not found to contribute significantly to the rate at which the particles float.
The aim of the second part of the flotation tests was to select the optimal pH, at which pyrite was depressed. Depression of pyrite in copper concentrate occurs at high pH. Lime is most often used to depress pyrite at pH 11 [19]. The amount of collector used in these tests was 84 g/t. Figure 3 and Table 5 show the results of flotation tests for different pH values. With increasing pH, Cu recovery in different concentrates increased. The very highest Cu recovery of 86.22 % was obtained at pH 11. The efficiency of individual flotations increased with increasing pH. The very highest efficiency of 55.98 % was achieved at pH 11, while the lowest efficiency of 14.15 % was at pH 8. The mass recovery of concentrate increased with increasing pH. The highest mass recovery 60.37 % was obtained at pH 11. In contrast, the lowest mass recovery at pH 8 was 40.0 %. With increasing pH, the Cu content in the concentrate decreased. At pH 8, the Cu content was 1.86 %, but at pH 11 only 1.25 %. Concurrently with increasing pH, the Cu enrichment in the concentrate decreased. At pH 8, the Cu enrichment was 1.88 %, but at pH 11 was 1.26 %.

![Figure 3. Results of flotation tests](image)

Rm - Cu recovery, SE_Cu - separation efficiency of Cu, v - mass recovery

| pH  | content Cu [%] | enrichment Cu [%] |
|-----|----------------|-------------------|
| 8   | 1.86           | 1.88              |
| 9   | 1.72           | 1.74              |
| 10  | 1.38           | 1.40              |
| 11  | 1.25           | 1.26              |

Table 5. Content of Cu and enrichment of Cu in the sample

Figure 4 shows the results of depressing pyrite at different pH values. With increasing pH, the content of pyrite in the concentrate decreased. At pH 8 the pyrite content of 9.26 %, but at pH 11 pyrite content was only 4.20 %. The lowest amount of pyrite was at pH 10, the content was 4.01 %. Based on the result, in which pyrite was depressed the best pH was 10. At pH 10 the greatest depressing of pyrite showed, wherein the content was 4.01 % and the content chalcopyrite in the concentrate was 13.16 %.
4 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 various dosages of collector on the flotation efficiency was observed. The second series of flotation was used to determine pH at which to achieve maximum depressing of pyrite. With increasing the dose of PAX collector, Cu recovery in individual concentrates increased. As a result, it turned out that the dose of 84 g/t PAX was the best dose for next flotation. As the pH of the medium increased, the pyrite content of the concentrate was reduced. The content pyrite in concentrate was 4.01 % for pH 10. Concurrently with increased pH, flotation efficiency increased. In the original polymetallic ore, the Cu content was 0.41 % after subsequent treatment and flotation tests, the Cu content was increased to 1.38 % with Cu recovery 86.18 %.

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REFERENCES

[1] BULATOVIC, S. M. Handbook of flotation reagents: chemistry, theory and practice. Boston: Elsevier Science, 2007. ISBN 978-0-444-53029-5.
[2] HUANG, P., L. WANG and Q. LIU. Depressant function of high molecular weight polyacrylamide in the xanthate flotation of chalcopyrite and galena. International Journal of Mineral Processing. 2014, 128, pp. 6-15. DOI: https://doi.org/10.1016/j.minpro.2014.02.004
[3] LEPPINEN, J.O, V.V HINTIKKA and R.P. KALAPUDAS. Effect of electrochemical control on selective flotation of copper and zinc from complex ores. Minerals Engineering. 1998, 11(1), pp. 39-51. DOI: https://doi.org/10.1016/S0892-6875(97)00137-4
[4] BAZIN, C. and M. PROULX. Distribution of reagents down a flotation bank to improve the recovery of coarse particles. International Journal of Mineral Processing. 2001, 61(1), pp. 1-12. DOI: https://doi.org/10.1016/S0301-7516(00)00022-3
[5] BOWDEN, J.L. and C.A. YOUNG. Xanthate chemisorption at copper and chalcopyrite surfaces. Journal of the Southern African Institute of Mining and Metallurgy. 2016, 116(6), pp. 503-508. DOI: http://dx.doi.org/10.17159/2411-9717/2016/v116n6a3
[6] BACH, L., R. D. NØRREGAARD, V. HANSEN and K. GUSTAVSON. Review on environmental risk assessment of mining chemicals used for mineral separation in the mineral resources industry and recommendations for Greenland. Aarhus University, Department of Bioscience, 2016, (203). Available from: http://dce2.au.dk/pub/SR203.pdf
[7] PIETRZYK, S. and B. TORA. Trends in global copper mining – a review. IOP Conference Series: Materials Science and Engineering. 2018, 427. DOI: https://iopscience.iop.org/article/10.1088/1757-899X/427/1/012002/meta

[8] DELBEKE, K. and P. H. RODRIGUEZ. Copper Concentrates: Environmental and Human Health hazard classification. Belgium: European Copper Institute, 2014.

[9] LIU, G., J. XIAO, H. REN and H. ZHONG. Adsorption thermodynamics and kinetics of N, N’-disopropoxypropyl-N”, N”-oxydiethylenedicarbonyl bis (thiourea) on chalcopyrite surfaces. Journal of Industrial and Engineering Chemistry. 2015, 21, pp. 1306-1313. DOI: https://doi.org/10.1016/j.jiec.2014.06.003

[10] OWUSU, C., K. QUAST and J. ADDAI-MENSAH. The use of canola oil as an environmentally friendly flotation collector in sulphide mineral processing. Minerals Engineering. 2016, 98, pp. 127-136. DOI: https://doi.org/10.1016/j.mineng.2016.08.003

[11] LOTTER, N.O., D.J. BRADSHAW and A.R. BARNES. Classification of the Major Copper Sulphides into semiconductor types, and associated flotation characteristics. Minerals Engineering. 2016, 96-97, pp. 177-184. DOI: https://doi.org/10.1016/j.mineng.2016.05.016

[12] KALEGOWDA, Y., Y. CHAN, D. WEI and S. L. HARMER. X-PEEM, XPS and ToF-SIMS characterisation of xanthate induced chalcopyrite flotation: Effect of pulp potential. Surface Science. 2015, 635, pp. 70-77.

[13] AGORHOM, E. A., W. SKINNER and M. ZANIN. Diethylenetriamine depression of Cu-activated pyrite hydrophobised by xanthate. Minerals Engineering. 2014, 57, pp. 36-42. DOI: https://doi.org/10.1016/j.mineng.2013.12.010

[14] HE, S., W. SKINNER and D. FORNASIERO. Effect of oxidation potential and zinc sulphate on the separation of chalcopyrite from pyrite. International Journal of Mineral Processing. 2006, 80(2-4), pp. 169-176. DOI: https://doi.org/10.1016/j.minpro.2006.03.009

[15] MUKUNGA, M. M. Recovery of copper and cobalt in the comparative flotation of a sulfide ore using xanthate and dithiophosphate as collectors. International Journal of Engineering and Applied Sciences (IJEAS). 2019, 6(7), pp. 26-29. DOI: https://dx.doi.org/10.31873/IJEAS.6.7.2019.06

[16] MINERAL PROCESSING FORMULAS: Concentration and Recovery Formulas. 911Metallurgist [online]. Canada: 911 Metallurgist, 2017 [cit. 2019-12-02]. Available from: https://www.911metallurgist.com/blog/milling-calculations-formulas

[17] WILLS, B. A. and J. A. FINCH. Introduction. Wills’ Mineral Processing Technology. 8. Elsevier, 2016, pp. 1-27.

[18] VIZCARRA, T.G., S.L. HARMER, E.M. WIGHTMAN, N.W. JOHNSON and E.V. MANLAPIG. The influence of particle shape properties and associated surface chemistry on the flotation kinetics of chalcopyrite. Minerals Engineering. 2011, 24(8), pp. 807-816. DOI: https://doi.org/10.1016/j.mineng.2011.02.019

[19] QIU, Z., G. LIU, Q. LIU, H. ZHONG and M. ZHANG. Separation of pyrite from chalcopyrite and molybdenite by using selective collector of N-isopropoxypropyl-N’-ethoxycarbonyl thiourea in high salinity water. Minerals Engineering. 2017, 100, pp. 93-98. DOI: https://doi.org/10.1016/j.mineng.2016.10.010