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BENEFICIATION OF ARSENIC BEARING COMPLEX SULPHIDE ORE BY FLOTATION

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Abstract: In this study beneficiation of a sulphide ore from the Gümüşhane-Black Sea Region of Turkey was investigated. Detailed flotation studies were carried out with the ore sample which contained 2.95% Pb, 6.72% Zn and 0.32% Cu. Mineralogical analyses showed that the sample includes pyrite, galena, sphalerite, chalcopyrite, tennantite, cerussite, anglesite and smithsonite. On the other hand, hematite, goethite, limonite, calcite and quartz were determined as gangue minerals. Selective sulphide concentrates with low arsenic content were tried to be produced by froth flotation. Individual concentrates of Pb, Zn and Cu assayed 67.54% Pb, and 61.49% Zn and 23.31% Cu where corresponding recoveries were 73.0% and 77.1% and 38.7%, respectively. Arsenic contents were less than 2000 ppm in the lead and zinc concentrates. Copper concentrate assayed 5.03% As since the major copper minerals were in tennantite form (copper arsenic sulphide mineral). In flotation tests, non-toxic reagents such as metabisulphite, caustified starch, and activated carbon were used to depress minerals in relevant circuits.

Key words: *arsenic, non-toxic depressants, sulphide minerals, flotation*

Introduction

The treatment processes for the beneficiation of copper-lead-zinc ores are generally complex. The methods used in the processing of copper-lead-zinc ore could be classified as follows (Bulatovic, 2007): a) sequential copper, lead, zinc flotation method where the copper, lead, and zinc are sequentially floated to produce separate copper, lead and zinc concentrates, b) bulk flotation of copper and lead followed by zinc flotation from the bulk tailings. The copper-lead separation is performed on the upgraded bulk concentrate. This is the most commonly used method in the treatment of copper-lead-zinc ores, c) bulk flotation of copper-lead-zinc minerals followed by a selective flotation of copper, lead and zinc from the bulk concentrate. This method is rarely used and is effective on the ores where the principal copper minerals are bornite, covellite and other secondary copper sulphides.

There is no general rule that can be prescribed as to which method is selected for the treatment of copper-lead-zinc ores.

Arsenic is one of the most hazardous inorganic pollutants for both the environment and human health. Therefore, discharge to the environment must be strictly controlled (Mandal et al., 2002). Minerals of copper with arsenic, which are enargite (Cu_3AsS_4), tennantite ($3\text{Cu}_2\text{S}\cdot\text{S}_{0.5}\cdot\text{As}_2\text{S}_3$), tetrahedrite ($3\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3$), do not have significant economic values. Furthermore, the existence of As in the concentrates requires payment of a penalty to the smelter. It is of economic and environmental interest to remove arsenic bearing minerals at an early stage of the process such as flotation (Ma and Bruckard, 2009).

Enargite, tennantite and tetrahedrite are usually secondary minerals to other copper sulphides. Flotation mechanisms of these minerals are not well understood since there are limited studies involved (Fornasiero et al., 2001; Smith and Brucard, 2007; Sasaki et al., 2010; Benzaazoua et al., 2002). Laboratory and plant practices showed that the flotation behaviour of enargite is similar to that of chalcocite. Tennantite and tetrahedrite do not respond well to flotation using xanthate as a collector. Tetrahedrite floats well with aerophine and mercaptan type of collectors at a pH value between 8 and 10 (Bulatovic, 2007).

Selective separation of sulphide minerals can be achieved using a variety of collectors and modifiers to adjust surface properties (Finkelstein, 1997; Yamamoto, 1980; Shen et al., 2001; Chandra and Gerson, 2009; Laskowski et al., 1991; 2007). In practice, when treating complex sulphide ores, the use of two or more depressants is common, especially when a selectivity problem is present or separation of several valuable minerals is required (Bulatovic and Wyslouzil, 1995).

Sulphur-oxy depressants are added to the flotation pulp in the form of sodium sulphite, sodium bi-sulphite, sodium metabisulphite or sulphur dioxide for the depression of pyrite, sphalerite and galena (Grano et al., 1997; 1997a; 1997b; Khmeleva et al.; 2003; 2005; 2006). Gül (2007) studied the effects of sodium meta bisulphite and activated carbon on the selective flotation of chalcopyrite from pyrite and successfully depressed pyrite while producing a high grade copper concentrate. Gül et al. (2008) used non-toxic reagents such as zinc sulphate, sodium meta bisulphite, caustic starch and activated carbon instead of highly toxic reagents like potassium bichromate and sodium cyanide, they obtained successful results for the separation of chalcopyrite, galena and sphalerite selectively.

This investigation focuses on producing individual concentrates of Pb and Zn with low arsenic contents from a complex sulphide ore employing non-toxic depressants to achieve selectivity.

Materials and methods

The ore sample was taken from Gümüşhane in Black Sea Region of Turkey. Mineralogical analyses show that the ore contains sphalerite (ZnS), galena (PbS), tennantite

($\text{Cu}_{12}\text{As}_4\text{S}_{13}$), chalcopyrite (CuFeS_2), cerussite (PbCO_3), anglesite (PbSO_4) and smithsonite (ZnCO_3). On the other hand pyrite, hematite, goethite, limonite, calcite and quartz were determined as gangue minerals. Figure 1 shows the mineralogical structure of the ore sample. Pyrite is generally seen as free and to some extent as locked particles whose average size is around 60 μm . In some cases pyrite has transformed to limonite. Sphalerite particles are generally seen to form irregular shapes and rarely replaced by pyrite. Sphalerite is the most abundant mineral in the ore after pyrite and it has an average particle size of 70 μm . Galena has irregular particle shapes with an average size of 60 μm . In the advanced cases of the replacement tennantite particles were locked in galena. Galena itself, on the other hand, was replaced by pyrite. Tennantite is generally observed as irregular particles and in some cases forms aggregates with other minerals. It usually fills the voids between pyrite particles though may enclose fine pyrite grains. Particle size of tennantite may vary between 10 and 300 μm . In Table 1 the results of chemical analysis of the ore sample are given.

Selective flotation experiments were carried out to obtain lead, zinc, copper and pyrite concentrates. Tests were conducted with samples ground below 0.1 mm employing a laboratory size ball mill. The final flotation flowsheet is presented in Fig. 2.

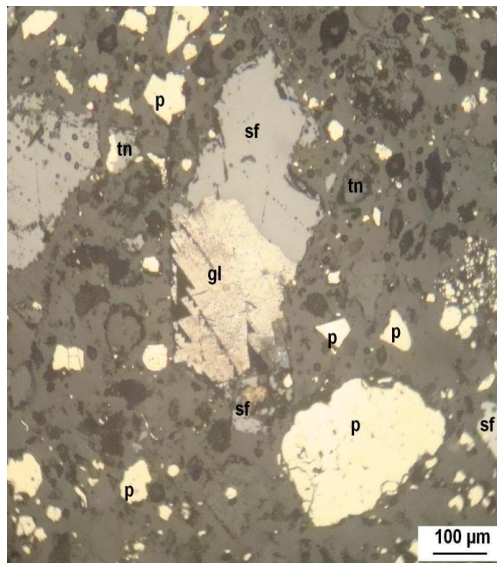


Fig. 1. Irregular shaped pyrite, sphalerite, galena and tennantite particles seen in the ore body

Table 1. Chemical analysis of the ore sample

Component	Assay, %
Pb	2.95
Zn	6.72
Cu	0.32
Fe	16.95
S	26.00
As	0.20
CaO	9.97
Al ₂ O ₃	2.38

It can be seen from Table 1 that the ore contains 2.95% Pb, 6.72% Zn, 0.32% Cu, and 0.20% As.

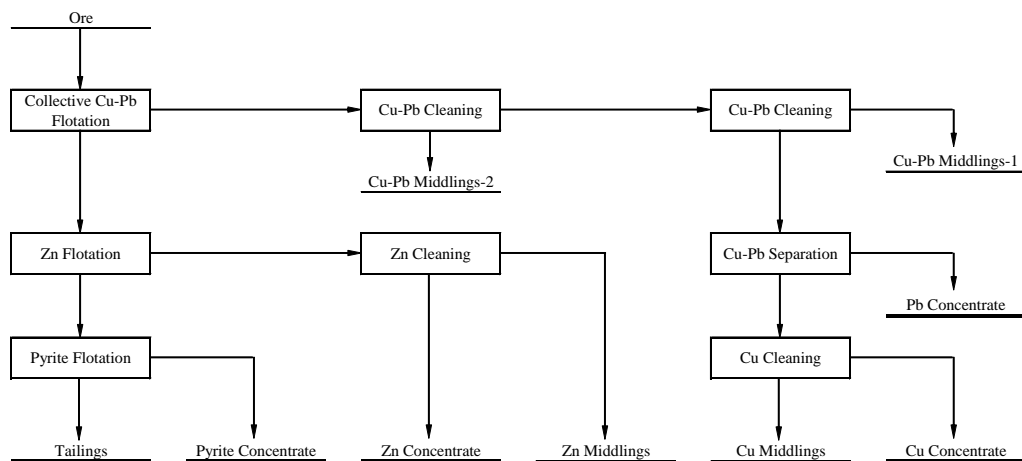


Fig. 2. Flotation flowsheet of experimental studies

Aerophine 3418-A was used as a collector in the Pb-Cu circuit whereas potassium amyl xanthate was the collector in the sphalerite-pyrite circuit. Sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) and ZnSO_4 were employed for the depression of sphalerite. Pyrite was deactivated by increasing pH by lime addition. Furthermore, $\text{Na}_2\text{S}_2\text{O}_5$ was added for the depression of pyrite. Sphalerite was later activated by CuSO_4 addition. In the selective flotation of copper minerals from galena the pulp was treated with activated carbon first and then sodium meta bisulphite and caustified starch were added to depress galena where copper was floated by the addition of small amounts of Aero 208. On the other hand, depressants like quebracho and S7260, that is a synthetic polymeric depressant were used in the Pb-Cu circuit to obtain selective concentrates (Cytec, 2002). Lime and sulfuric acid were the reagents to control the pulp pH. In this investi-

gation the effect of pH, collector dosage, the number of flotation stages, depressant type and dosage were studied on the selective concentration of Cu, Pb and Zn minerals in the ore sample.

Results and discussions

Flotation tests were carried out to obtain selective concentrates of Pb, Zn, and Cu. The procedure adopted was to float Pb-Cu collectively first leaving Zn in the sink and then to activate Zn using conventional methods. Pb-Cu separation from the bulk concentrate was achieved by depressing Cu and floating Pb minerals. The flotation conditions and test results are presented in Tables 2 and 3, respectively.

Table 2. Flotation test conditions

Collective Cu-Pb Flotation		Zn Flotation	
Na ₂ S ₂ O ₅ , g/Mg	1500	CuSO ₄ , g/Mg	300
ZnSO ₄ , g/Mg	2250	KAX, g/Mg	50
Aerophine 3418 A, g/Mg	35	MIBC, g/Mg	70
MIBC, g/Mg	80	pH	11.0
pH	9.0	Zn Cleaning	
Cu-Pb Separation		KAX, g/Mg	2.5
Quebracho, g/Mg	50	MIBC, g/Mg	10
S7260, g/Mg	25	pH	11.0
Aerophine 3418 A, g/Mg	5	Pyrite Flotation	
MIBC, g/Mg	2.5	KAX, g/Mg	200
pH	9.0	MIBC, g/Mg	60
		pH	4.5-5.0

Table 3. The results of selective flotation using Quebracho and S7260

Products	Weight %	Pb, %		Zn, %		Cu, %	
		Assay	Recovery	Assay	Recovery	Assay	Recovery
Pb Concentrate	3.0	52.44	51.7	7.08	3.3	5.05	43.1
Cu-Pb Middlings 1	0.9	44.03	13.0	8.34	1.2	2.40	6.1
Cu-Pb Middlings 2	2.4	19.30	15.2	7.39	2.7	1.88	12.8
Zn Concentrate	9.4	1.02	3.2	60.77	88.2	0.38	10.2
Zn Middlings	1.2	2.85	1.1	6.20	1.2	0.83	2.8
Pyrite Concentrate	36.5	0.57	6.9	0.36	2.0	0.19	19.7
Tailings	46.6	0.58	8.9	0.20	1.4	0.04	5.3
Total	100.0	3.04	100.0	6.48	100.0	0.35	100.0

S7260 and Quebracho were used to depress copper minerals and pyrite in the bulk Pb-Cu concentrate. However, the attempt to depress Cu minerals was not a success and consequently Pb concentrate assayed 5.05% Cu. Zinc concentrate, on the other hand, was obtained with 60.77% Zn content and 88.2% recovery. Since zinc was successfully concentrated with relatively high recoveries and grades, in the proceeding tests attention was given to the separation of Pb from Cu and As and conditions in the zinc circuit were not further studied.

In the following experiments alternative procedures were studied to obtain a clean Pb concentrate. The rougher Pb-Cu bulk concentrate was cleaned twice employing $ZnSO_4$ and $Na_2S_2O_5$ as depressants. In the separation of Pb from Cu, all minerals were depressed first using activated carbon, $Na_2S_2O_5$ and caustified starch and Cu was floated by the addition of small amounts of Aero 208 which is particularly synthesized for Cu. Flotation conditions and results of selective flotation for the Pb-Cu separation are given in Tables 4 and 5, respectively.

Table 4. Flotation conditions for separation of Pb from Cu

Collective Cu-Pb Flotation		Cu-Pb Separation	
$Na_2S_2O_5$, g/Mg	1500	Activated Carbon, g/Mg	250
$ZnSO_4$, g/Mg	2250	$Na_2S_2O_5$, g/Mg	500
Aerophine 3418 A, g/Mg	50	Caustified Starch, g/Mg	100
MIBC, g/Mg	60	Aero 208, g/Mg	6
pH	9.0	MIBC, g/Mg	6
Cu-Pb Cleaning		pH	6.0
$Na_2S_2O_5$, g/Mg	375		
$ZnSO_4$, g/Mg	750		
MIBC, g/Mg	2.5		
pH	9.0		

Table 5. Results of flotation for Pb-Cu separation

Products	Weight %	Pb, %		Zn, %		Cu, %	
		Assay	Recovery	Assay	Recovery	Assay	Recovery
Pb Concentrate	3.7	65.52	76.0	7.16	4.7	0.77	9.1
Cu-Pb Middlings	0.9	19.29	5.4	3.50	0.6	15.73	44.9
Cu-Pb-Zn Middlings 1	0.8	3.87	1.0	18.40	2.6	2.97	7.5
Cu-Pb-Zn Middlings 2	2.6	3.23	2.6	16.50	7.7	1.13	9.3
Tailings	92.0	0.52	15.0	5.14	84.4	0.10	29.2
Total	100.0	3.19	100.0	5.60	100.0	0.32	100.0

The lead concentrate produced meets the specifications of smelters in terms of Pb and Cu contents. Furthermore, Pb recovery is at an acceptable level. Therefore, the results in Table 5 prove that separation is successful between lead and copper. In order

to check the reproducibility of the experiment and to produce a copper concentrate another test was conducted under the experimental conditions seen in Table 6 and the results are presented in Table 7.

Table 6. Experimental conditions to produce selective Pb and Cu concentrates

Collective Cu-Pb Flotation		Cu-Pb Cleaning	
Na ₂ S ₂ O ₅ , g/Mg	1500	Na ₂ S ₂ O ₅ , g/Mg	375
ZnSO ₄ , g/Mg	2250	ZnSO ₄ , g/Mg	750
Aerophine 3418 A, g/Mg	50	MIBC, g/Mg	2.5
MIBC, g/Mg	60	pH	9.0
pH	9.0	Cu Cleaning	
Cu-Pb Separation		Without any reagents	
Activated Carbon, g/Mg	250	Zn Flotation	
Na ₂ S ₂ O ₅ , g/Mg	500	CuSO ₄ , g/Mg	300
Caustified Starch, g/Mg	100	KAX, g/Mg	40
Aero 208, g/Mg	6	MIBC, g/Mg	50
MIBC, g/Mg	6	pH	11.0
pH	6.0	Zn Cleaning	
Pyrite Flotation		KAX, g/Mg	2.5
KAX, g/Mg	200	MIBC, g/Mg	10
MIBC, g/Mg	60	pH	11.0
pH	4.5-5.0		

Copper was floated using Aero 208 from the bulk Pb-Cu concentrates and then cleaned without any reagents addition.

Table 7. Results of selective flotation

Products	Weight %	Pb, %		Zn, %		Cu, %		As, %	
		Assay	Rec.	Assay	Rec.	Assay	Rec.	Assay	Rec.
Pb Concentrate	3.7	67.54	73.0	8.72	5.3	0.59	6.0	0.16	2.9
Cu Concentrate	0.6	12.65	2.2	3.18	0.3	23.31	38.7	5.03	14.9
Cu Middlings	0.5	46.26	6.8	5.51	0.4	2.78	3.8	0.54	1.3
Cu-Pb Middlings 1	0.8	6.03	1.4	21.30	2.8	2.86	6.3	0.55	2.2
Cu-Pb Middlings 2	2.5	4.65	3.4	20.31	8.3	1.73	12.0	0.99	12.3
Zn Concentrate	7.7	0.58	1.3	61.49	77.1	0.28	6.0	0.05	1.9
Zn Middlings	1.6	1.97	0.9	10.89	2.8	1.39	6.2	0.49	3.9
Pyrite Concentrate	36.5	0.52	5.5	0.27	1.6	0.17	17.2	0.31	56.0
Tailings	46.1	0.41	5.5	0.19	1.4	0.03	3.8	0.02	4.6
Total	100.0	3.43	100.0	6.14	100.0	0.36	100.0	0.20	100.0

Rec.: Recovery

It can be seen from Table 7 that a Pb concentrate could be obtained with 67.54% content and 73.0% recovery. The relationship between Cu and As contents are seen in Table 7 hence As assay in the Pb concentrate is closely related to the Cu content. Zinc concentrate was produced with 61.49% content and 77.1% recovery. Copper content in Zn concentrate is 0.28%, and As is 0.05%. Copper minerals are seen to be depressed effectively, consequently arsenic content decreases in Pb and Zn concentrates. Furthermore a copper concentrate is obtained with 23.31% Cu content and 38.7% recovery while As content is 5.03% as expected. It is suggested that high As content copper concentrates could be heat treated to get rid of As. Therefore, the concentrate is roasted at low temperatures, so that the arsenic is selectively fumed off into a low-volume stream product leaving a calcined product rich in copper and sulphur. In the final stage, arsenic in the fumes is immobilised in a low temperature ceramic such that safe disposal back into the soil is possible (Jahanshahi et al., 2006; Bruckard et al.; 2010).

Some depressants used in the conventional selective flotation of sulphide ores are extremely toxic and must be avoided as much as possible. In this study the use of non-toxic reagents such as $ZnSO_4$, sodium metabisulphite ($Na_2S_2O_5$), caustified starch and activated carbon instead of highly toxic conventional reagents such as $K_2Cr_2O_7$ and NaCN provided successful results for the selective flotation of galena, sphalerite, tenatite and pyrite.

The mechanism of $ZnSO_4$ to depress sphalerite is well known. Possible deactivation mechanisms regarding sodium metabisulphite and caustified starch are presented in the introduction yet the usage of starch must be clearly monitored since excess amounts will depress all minerals. Starch deactivates minerals through reactions with metal oxides or hydroxides on the surface. It is also reported that it can attach to the surface by hydrophobic forces (Liu et al.; 2000; Bıçak and Ekmekci; 2005). Activated carbon, however, is not a direct depressant for sulphide minerals; it actually adsorbs excess amounts of collector species. Activated carbon in this study was used for the selective flotation of chalcopyrite from galena. When it was added to the flotation pulp, excess amount of collector was adsorbed thus reducing the concentration of collector in the solution. On decreasing the collector concentration in the solution by adding activated carbon, the collector desorbs off the surface of galena and hence depression is facilitated.

Conclusions

1. This investigation conducted with a Pb-Cu-Zn ore sample collected from Gümüşhane (Turkey) has proven that it is possible to selectively separate As containing copper minerals from galena and sphalerite using non-toxic reagents.
2. Separate lead and zinc concentrates were produced assaying 67.54% Pb, 61.49% Zn with 0.16% and 0.05% As, respectively, that are much lower than the smelter requirement of 2000 ppm.

3. As a result of this investigation As being an environmental pollutant was eliminated to acceptable levels in Pb and Zn concentrates employing non-toxic reagents as an alternative to high toxic conventional chemicals.

References

- BENZAAZOOUA M., MARION P., LIOUVILLE-BOURGEOIS L., JOUSSEMET R., HOUOT R., FRANCO A., PINTO A., 2002, *Mineralogical distribution of some minor and trace elements during a laboratory flotation processing of Neves-Corvo ore (Portugal)*, International Journal of Mineral Processing, 66, No. 1–4, 163.
- BICAK O., EKMEKCI Z., 2005, *Polisakkaritlerin flotasyonda bastırıcı olarak kullanımı ve soğurum mekanizmaları*, Madencilik, 44, No. 1, 19 (In Turkish).
- BRUCKARD W.J., DAVEY K.J., JORGENSEN F.R.A., WRIGHT S., BREW D.R.M., HAQUE N., VANCE E. R., 2010, *Development and evaluation of an early removal process for the beneficiation of arsenic-bearing copper ores*, Mining Engineering, 23, No. 15, 1167.
- BULATOVIC S., WYSLOUZIL D.M., 1995, *Selection and evaluation of different depressants systems for flotation of complex sulphide ores*, Minerals Engineering, 8, No. 1–2, 63.
- BULATOVIC S.M., 2007, *Handbook of flotation reagents, chemistry. theory and practice, flotation of sulfide ores*, Elsevier, Amsterdam.
- CHANDRA A.P., GERSON A.R., 2009, *A review of the fundamental studies of the copper activation mechanism for selective flotation of sulfide minerals, sphalerite and pyrite*, Advances in Colloid and Interface Science, 145, 97.
- Cytec mining chemical handbook*, 2002, Horton Printing Company, Meriden.
- FINKELSTEIN N.P., 1997, *The activation of sulphide minerals for flotation: a review*, International Journal of Mineral Processing, 52, No. 2–3, 81.
- FORNASIERO D., FULLSTON C.L., RALSTON J., 2001, *Separation of enargite and tennantite from non-arsenic copper sulfide minerals by selective oxidation or dissolution*, International Journal of Mineral Processing, 61, No. 2, 109.
- GRANO S.R., SOLLAART M., SKINNER W., PRESTIDGE., RALSTON J., 1997, *Surface modifications in the chalcopyrite-sulphite ion system. I. collectorless flotation, XPS and dissolution study*, International Journal of Mineral Processing, 50, No. 1–2, 1.
- GRANO S.R., JOHNSON N.W., RALSTON J., 1997a, *Control of the solution interaction of meta bisulphite and ethyl xanthate in the flotation of the Hilton ore of Mount Isa Mines Limited*, Australia, Mineral Engineering, 10, No. 1, 17.
- GRANO S.R., PRESTIDGE C.A., RALSTON J., 1997b, *Solution interaction of ethyl xanthate and sulphite and its effect on galena flotation and xanthate adsorption*, International Journal of Mineral Processing, 52, 161.
- GÜL A., 2007, *The role of Na₂S₂O₃ and activated carbon on the selective flotation of chalcopyrite from a copper ore using a dithiophosphine-type collector*, Mineral Processing, Extractive Metal.Rev., 28, 235.
- GÜL A., YÜCE A.E., SIRKECI A.A., OZER M., 2008, *Use of non-toxic depressants in the selective flotation of copper lead-zinc ores*, Canadian Metallurgical Quarterly, 47, No. 2, 111.
- JAHANSHAHI S., BRUCKARD W.J., CHEN C., JORGENSEN F.R.A., 2006, *Management of minor elements in the production of basemetals*, in: Green Processing 2006, 3rd International Conference on the Sustainable Processing of Minerals, Newcastle, Australia, The Australasian Institute of Mining and Metallurgy, Melbourne, 2006, 25.

- KHMELEVA T.N., BEATTIE D.A., GEORGIEV T.V., SKINNER W.M., 2003, *Surface study of the effect of sulphite ions on copper-activated pyrite pre-treated with xanthate*, Mineral Engineering, 16, 601.
- KHMELEVA T.N., SKINNER W.M., BEATTIE D.A., 2005, *Depression mechanisms of sodium bisulphite in the xanthate-collectorless flotation of copper activated sphalerite*, International Journal of Mineral Processing, 76, 43.
- KHMELEVA T.N., CHAPELET J.K., SKINNER W.M., BEATTIE D.A., 2006, *Depression mechanisms of sodium bisulphite in the xanthate-induced flotation of copper activated sphalerite*, International Journal of Mineral Processing, 79, 61.
- LASKOWSKI J.S., LIU Q., BOLIN N.J., 1991, *Polysaccharides in flotation of sulphides. Part 1. Adsorption of polysaccharides onto mineral surfaces*, International Journal of Mineral Processing, 33, No. 1–4, 223.
- LASKOWSKI J.S., LIU Q., O'CONNOR T., 2007, *Current understanding of the mechanism of polysaccharide adsorption at the mineral /aqueous solution interface*, International Journal of Mineral Processing, 84, 59.
- LIU Q., ZHANG Y., LASKOWSKI J. S., 2000, *The adsorption of polysaccharides onto mineral surfaces: an acid/base interaction*, International Journal of Mineral Processing, 60, p. 229.
- MA X., BRUCKARD W.J., 2009, *Rejection of arsenic minerals in sulfide flotation — A literature review*, International Journal of Mineral Processing, 93, No. 2,1, 89.
- MANDAL B. K., SUZUKI K. T., 2002, *Arsenic round the worlds: a review*, Talanta, 58, 201.
- SASAKI K., TAKATSUGI K., ISHIKURA K., HIRAJIMA T., 2010, *Spectroscopic study on oxidative dissolution of chalcopyrite, enargite and tennantite at different pH values*, Hydrometallurgy 100, 144.
- SHEN W.Z., FORNASIERO D., RALSTON J., 2001, *Flotation of sphalerite and pyrite in the presence of sodium sulfite*, International Journal of Mineral Processing, 63, No. 1, 17.
- SMITH L.K., BRUCKARD W. J., 2007, *The separation of arsenic from copper in a Northparkes copper–gold ore using controlled-potential flotation*, International Journal of Mineral Processing, 84, 15.
- YAMAMOTO T., 1980, *Mechanism of depression of pyrite and sphalerite by sulphite*, Complex sulphide ores, ed. M. J. Jones, London, Institute of Mining and Metallurgy, 71.