SELECTIVITY AND POWER OF FROTHERS
IN COPPER ORE FLOTATION [*]

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Abstract: Froth flotation is widely used for upgrading of ores and other materials. Efficiency of flotation depends on many parameters, including type, chemical structure and dose of flotation reagents. Selection of a proper frother in flotation depends on the material used, necessary dose of frother and its selectivity. The selectivity of flotation can be characterized by proper separation factors and indices. In this paper separation selectivity and power of frothers were evaluated basing on separation data for a given material and frother, plotted as the recovery of the useful component in the concentrate versus the recovery of the remaining components in the tailing. Such a plot is called the Fuerstenau upgrading curve. The selectivity was defined as the location of the whole upgrading curve in relation to no and ideal separation lines, expressed on the scale from 50 (no separation) to 100% (ideal separation). In turn, the flotation power was defined as the dose of frother to reach a certain upgrading level at which recoveries of the useful component in the concentrate and unwanted components in the tailing are equal. The power and selectivity of frothers were determined for the Kupferschiefer stratiform copper ore floated in the presence of a fixed amount of xanthate and varying doses of frothers using a laboratory flotation machine. Basing on the separation results for different poly(propylene glycol) and poly(ethylene glycol) alkyl ethers, it was found that the concentrate yield and recovery of copper as the useful component in the concentrate were greatly influenced by the type and dose of frother. However, the same results plotted in the form of the Fuerstenau upgrading curve clearly indicated that the selectivity of frothers was similar, while their power was not always the same. It proves that both selectivity and power of frothers are useful parameters for characterizing flotation systems.

Keywords: flotation, frother, separation, selectivity, power, copper ore, upgrading curve, Fuerstenau curve

Introduction

Frothers, due to their ability to form foam and froth, make a flotation process possible. Properties of frothers depend on many parameters, including their structure, dose and

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interactions with other flotation reagents. Frothers also determine outcomes of flotation (Heyes and Trahar, 1977; Malysa et al., 1987; Jia et al., 2002; Drzymala, 2005; Melo and Laskowski, 2006; Gupta et al., 2007; Kowalczuk et al., 2014; 2016). Frothers are usually divided into powerful and selective (Laskowski et al., 2003; Laskowski, 2004). This classification is based either on the ability of a frother to form foam in a two phase water-gas system characterized by critical coalescence concentration (CCC) (Cho and Laskowski, 2002; Zhang et al., 2012; Kowalczuk, 2013) and dynamic foamability index (DFI) (Czarnecki et al., 1982; Khoshdast et al., 2015) or pure frother properties such as hydrophilic-lipophilic balance (HLB) and molecular weight (MW) (Laskowski, 2004). Laskowski (2004) suggested that the powerful frothers have low values of CCC and high DFI producing stable foams and could be used in flotation of coarse particles, while selective ones, with high values of CCC and low DFI, provide better performance in flotation of fine particles. However, the ability of frother to form foam is a two-phase parameter, while formation of froth during flotation is a three-phase phenomenon. Moreover, most flotation are multiphase (more than one solid) systems. Therefore, another definitions of selectivity and power of frothers used in flotation seem to be necessary. In our opinion it should be based on upgrading curves which relate two separation results parameters. One of many possible separation curves (Drzymala, 2006; Miller et al., 2009; Neethling and Cilliers, 2008) is the Fuerstenau upgrading plot. This curve is very powerful and useful since it simultaneously monitors the recoveries of useful and unwanted components of beneficiated material. In addition to that, the plot has a useful geometrical form making it easy to apply different mathematical equations for approximation of separation results (Drzymala and Ahmed, 2005).

In this work, separation selectivity and power of frothers will be evaluated basing on separation data plotted in the form of the Fuerstenau upgrading curve as the recovery of useful component (copper) in the concentrate versus the recovery of remaining components in the tailing. The comparison and assessment of frothers will be based on results of flotation of the Kupferschiefer stratiform copper ore in the presence of a fixed amount of xanthate (100 g/Mg) and varying doses of poly(propylene glycol) (C_nP_m) and poly(ethylene glycol) (C_nE_m) alkyl ethers frothers.

Materials and methods

The Kupferschiefer stratiform copper ore from Legnica-Glogow Zechstein Copper Ore Basin located in Lubin (SW Poland) was used in the investigations. The ore consisted of three lithological components, that is dolomite, carbonaceous shale and sandstone (Drzymala et al., 2013). The mineralogical analysis showed that the ore contained chalcopyrite, bornite and chalcocite as the sulfide copper-bearing minerals, galena as the lead-bearing mineral as well as quartz, clay and carbonate minerals. The average content of copper in the feed was 0.78±0.2%.

The ore was crushed in a jaw crusher to obtain particles smaller than 1 mm in size. Prior to each flotation experiment, the crushed material was wet ground in a steel ball mill. The size distribution of the ore, used as the flotation feed, is presented in Table 1.

Table 1. Feed size distribution

Size, μm	Mass, g	Mass, %	Cumulative mass, %
-40	18.4	72.7	72.7
+40-71	5.9	27.3	96.0
+71	1.0	4.0	100.00
Total	25.3	100.0	

Each copper ore sample was floated in tap water and in the presence of fixed amount of potassium ethyl xanthate (KEtX) (100 g/Mg) as well as varying doses of poly(propylene glycol) C_nP_m and poly(ethylene glycol) C_nE_m alkyl ethers frothers. The flotation reagents used in this work were obtained from Sigma-Aldrich ($\geq$99% purity) and were used without further purification. Table 2 shows the properties of frothers used in this work, including numbers of alkyl (n) and either propylene or ethylene glycol (m) groups.

Table 2. Characterization of non-ionic frothers used in flotation of copper ore.
CCC$_{95}$ data of Finch and Zhang (2014)

Frother	Symbol	n	m	MW, g/mol	CCC$_{95}$, mM
poly(propylene glycol) alkyl ethers $C_nH_{2n+1}O(C_3H_6O)_mH$ (C_nP_m)	C_4P_3	4	3	248.36	0.029
	C_3P_3	3	3	234.33	0.045
	C_1P_3	1	3	206.28	0.073
	C_0P_3	0	3	192.25	0.17
poly(ethylene glycol) alkyl ethers $C_nH_{2n+1}O(C_2H_4O)_mH$ (C_nE_m)	C_4E_1	4	1	118.17	0.12
	C_4E_2	4	2	162.23	0.11
	C_6E_2	6	2	190.29	0.068
	C_4E_3	4	3	206.28	0.11

Flotation experiments were conducted in a laboratory Mekhanobr type sub-aeration flotation machine equipped in a 1.0 dm^3 Plexiglas cell. A feed of 300 g and tap water were mixed together and agitated for one minute in the flotation cell before adding any reagent. After collector (KEtX) addition, the pulp was conditioned for 3 min and an additional one minute with a frother. The total time of flotation was 16 min in each tests. The flotation products were dried in an oven at 105 °C for 24 h, weighted to determine the concentrate yield, next homogenized and subjected to chemical analyses for copper. The samples were analyzed by using energy dispersive X-ray fluorescence (EDXRF).

All flotation experiments were carried out at ambient temperature (20-22 °C) and natural pH of solutions (7.8-8.2). In each flotation test the air flow rate (60 dm^3/h) and the stirring speed (2600 rpm) were kept constant.

Results and discussion

The flotation tests were performed to investigate the influence of the type and dosage of poly(propylene glycol) (C_nP_m) and poly(ethylene glycol) (C_nE_m) alkyl ether frothers on the flotation performance of the Kupferschiefer stratiform copper ore. The simplest approach to evaluate the obtained results and compare flotation properties of the used frothers is plotting the data in the form of concentrate yield and copper recovery, both as a function of frother dose. Such plots are shown in Figs. 1 and 2, respectively. Since it is unclear what concentration unit should be used to compare the frothers, the concentration is expressed in two different forms, that is in mmol/dm^3 and mg/dm^3.
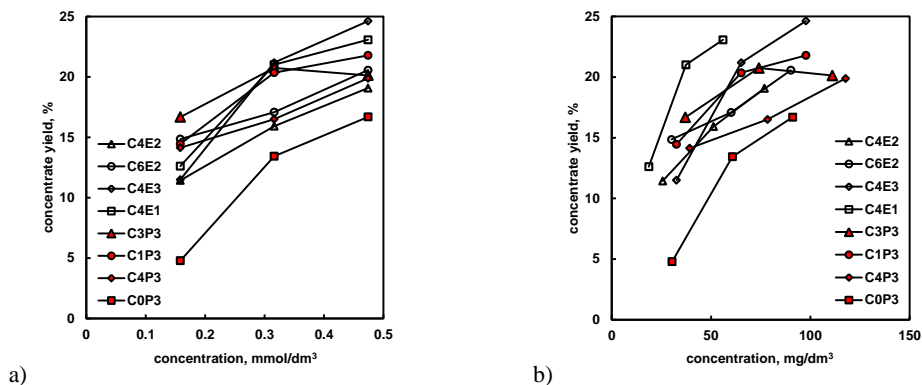

Fig. 1. Concentrate yield vs. frother dose expressed in (a) mmol/dm^3
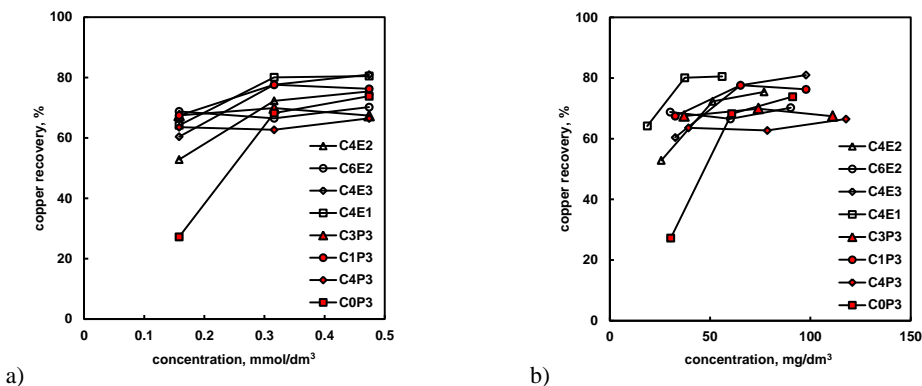and (b) mg/dm^3 after 16 min of flotation

Fig. 2. Copper recovery vs. frother dose expressed in (a) mmol/dm^3
and (b) mg/dm^3 after 16 min of flotation

Figures 1 and 2 show that the concentrate yield (Fig. 1) and copper recovery (Fig. 2) are dependent on the type and dose (concentration) of frother. Higher frother dose yielded higher mass and copper recoveries. The flotation results seem to also depend on the concentration unit ($mmol/dm^3$ or mg/dm^3) used for comparing the results. Figures 1 and 2 show that the lowest yield and copper recovery were obtained with tri(propylene glycol) (C_0P_3), tri(propylene glycol) butyl ether (C_4P_3), while the highest with tri(ethylene glycol) monobutyl ether (C_4E_3), (ethylene glycol) monobutyl ether (C_4E_1) and tri(propylene glycol) methyl ether (C_1P_3). The diminished flotation performance with C_0P_3 and C_4P_3 frothers was probably related to their low dose used in the upgrading process. On the other hand, the enhanced flotation performance with C_4E_3, C_4E_1 and C_1P_3 frothers can be attributed to the more stable froth. Frothers which produce more stable foam/froth are also more efficient in reducing bubble size (Laskowski, 2004). It should be also emphasized here that when the frother concentration is expressed in mg/dm^3, the enhanced concentrate yield with C_4E_3 and C_1P_3 frothers were achieved at higher concentration (100 mg/dm^3) (Fig.1b) when compared to the C_4E_1 frother. However, when the frother concentration is expressed in $mmol/dm^3$, C_4E_3 and C_4E_1 act similarly. The experimental results demonstrated that C_4E_1 and C_4E_3 frothers floated well (Cu recovery 80%) copper-bearing minerals present in the ore, that is chalcopyrite, bornite and chalcocite, at relatively low concentration, while for C_1P_3 frother the same copper recovery, equal to 80%, was possible only at higher dose expressed in mg/dm^3. It means that the power of C_4E_1 expressed in mg/dm^3 was greater than C_1P_3 and it was the greatest among all tested in this work frothers. A substantially lower dose of C_4E_1 frother expressed in considerably mg/dm^3 means reduced cost of industrial flotation.

There are many shortcomings of plotting separately yield and recovery of useful component in the concentrate for evaluation of frothers: *i*) the results are shown in two different graphs; *ii*) it is not obvious what unit of frother concentration ($mmol/dm^3$, mg/dm^3, g/Mg) should be used; *iii)* the plots form a cloud of lines. Therefore, another approach of frothers assessment is proposed. It is based on the concept of selectivity and power of flotation frothers. However, the definitions of these parameters are different from those proposed by Laskowski et al. (2003). The proposed here method is based on the Fuerstenau upgrading curve relating the recovery of the useful component (in our case copper) in the concentrate versus the recovery of the remaining (non-copper) components in the tailing. The selectivity and power indicators are based on the whole upgrading curve, not just on an arbitrarily chosen point. Selectivity *F*, is the point at which the upgrading curve crosses the ascending diagonal of the plot (Fig. 3). Selectivity *F* can also be determined mathematically by approximation of all experimental data for given flotation with suitable equations (Drzymala and Ahmed, 2005).
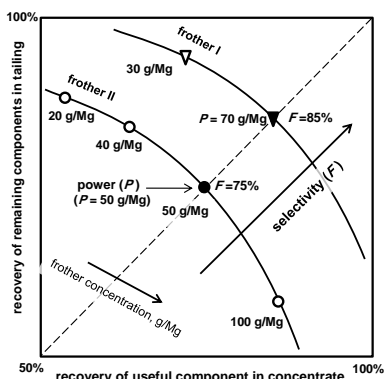
Fig. 3. Hypothetical Fuerstenau upgrading curve to show selectivity F (%)
and power P (g/Mg) of flotation frothers

The selectivity F index increases when the separation curve moves towards the ideal separation line and its scale is from 50% for no separation to 100% for ideal separation. It should be noted that selectivity indicator F assumes values from 0 to 50 for degrading. Selectivity F is in fact a global, not local, selectivity index because it combines two, not easy to use simultaneously, separation parameters such as the recovery of the useful component (here copper) in the concentrate and the recovery of the remaining components in the tailing.

The power of frother (P) is also determined from the Fuerstenau upgrading curve and is defined as the reagent dose (expressed in either mmol/dm^3, mg/dm^3 or g/Mg) of frother needed to reach a certain degree of separation. The most convenient approach is to use the point when the recovery of the useful component in the concentrate is equal to the recovery of the remaining components in the tailing (Fig. 3). It should be noted that when the experimental points are located on the right side of diagonal, that is a line joining points 0:0 and 100:100, the frother is overdosed. Overdosing of frothers could cause a high recovery with low selectivity, and therefore cost-ineffective flotation in industry

The new approach of selectivity and power was used for evaluation of the tested in this work frothers in flotation of the Kupferschiefer stratiform copper ore. Figures 4 a-c show the results of flotation plotted in the form of the Fuerstenau upgrading curve. Selectivity F was determined using a one-adjustable parameter mathematical equation which provided very accurate approximation of all obtained experimental data points (Drzymala and Ahmed, 2005):

$$\varepsilon_r = \left(\frac{F^2}{2F-100} \right) \frac{(100-\varepsilon)}{\left(\dfrac{F^2}{2F-100} - \varepsilon \right)} . \tag{1}$$
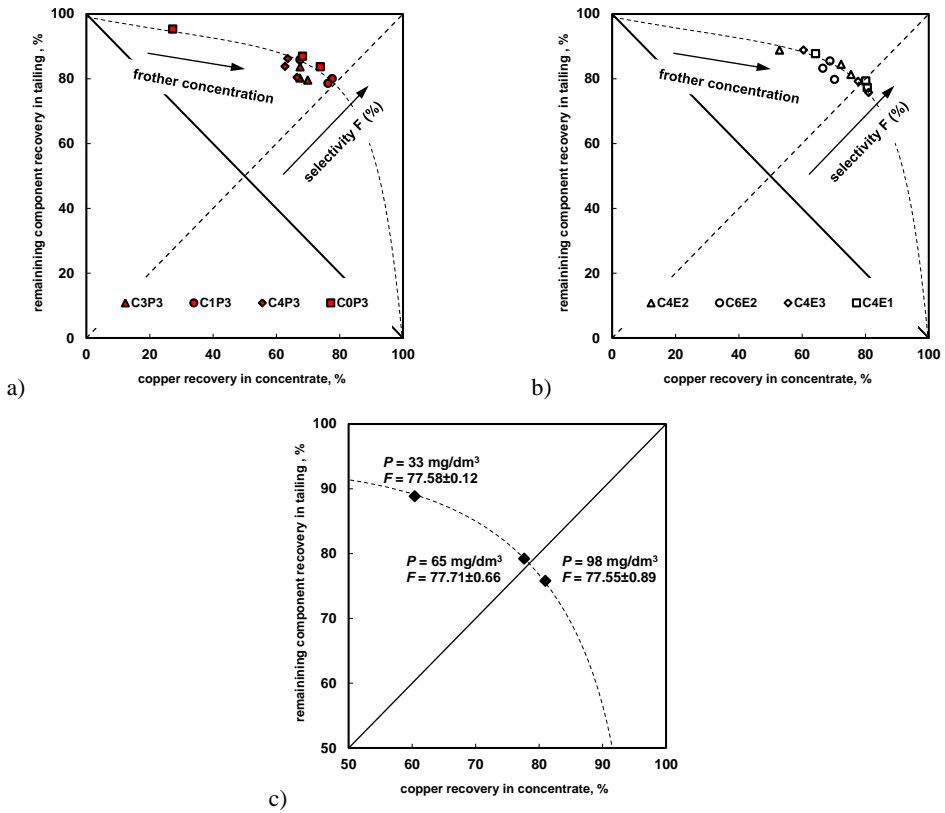
a)

b)

c)

Fig. 4. Fuerstenau upgrading curves for flotation of copper ore
in the presence of (a) poly(propylene glycol) alkyl ethers, (b) poly(ethylene glycol) alkyl ethers
and (c) C_4E_3 as an example. Experimental data points were approximated with Eq. 1.

The obtained values of selectivity F (in %) and power P (expressed either in mg/dm^3 or mmol/dm^3) of all tested in this work frothers are presented in Fig. 5. It contrast to the cloud of lines in the case of evaluation of the flotation performance using the yield and recovery lines separately, Fig. 5 clearly shows that determined selectivity F of all tested frothers is similar (76±2%), while their power P is different. As can be judged from P values expressed in mg/dm^3 and given in Fig. 5, the best and cost-effective frothers used in flotation of the Kupferschiefer stratiform copper ore were C_4E_1, C_4E_3 and C_1P_3. Frothers C_4E_1 and C_4E_3 were also found to be the most selective ones for flotation of carbonaceous copper-bearing shale (Kowalczuk et al., 2015), which together with dolomitic and sandstone lithological layers forms the Kupferschiefer stratiform copper ore.
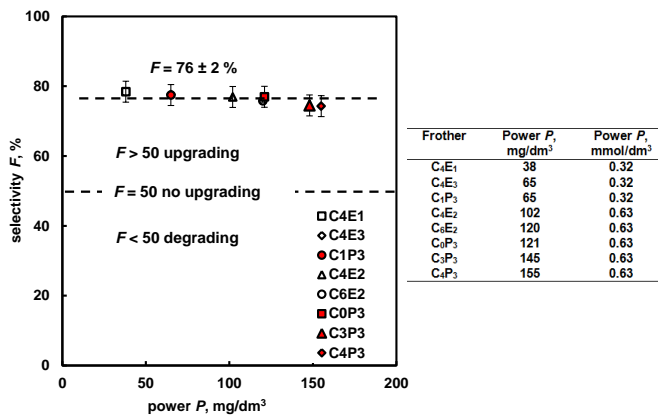
Frother	Power P, mg/dm^3	Power P, mmol/dm^3
C$_4$E$_1$	38	0.32
C$_4$E$_3$	65	0.32
C$_1$P$_3$	65	0.32
C$_4$E$_2$	102	0.63
C$_6$E$_2$	120	0.63
C$_0$P$_3$	121	0.63
C$_3$P$_3$	145	0.63
C$_4$P$_3$	155	0.63

Fig. 5. Selectivity F (76±2%) and power P
(in mg/dm^3 and mmol/dm^3) of tested frothers

Conclusions

The investigated in this work frothers from the poly(propylene glycol) and poly(ethylene glycol) alkyl ethers families can be successfully used in flotation of the Kupferschiefer stratiform copper ore. It was found that the concentrate yield and copper recovery were greatly influenced by the type and dose of frother. However, the same results plotted in the form of the recovery-recovery Fuerstenau upgrading curve provided not only well organized separation results, but also, using special definitions, selectivity F and power P of frothers. The obtained indices clearly indicated that the selectivity of all frothers used in the work was similar, while their power was not always the same. It proves that both proposed indices, that is frother selectivity and frother power are useful parameters for characterizing flotation systems.

Acknowledgments

References

CHO Y.S., LASKOWSKI J.S. (2002). *Effect of flotation frothers on bubble size and foam stability*. International Journal of Mineral Processing, 64, 69–80.

CZARNECKI J., MALYSA K., POMIANOWSKI A. (1982). *Dynamic frothability index*. Journal of Colloid and Interface Science, 86(2), 570–572.

DRZYMALA J. (2005). *Evaluation and comparison of separation performance for varying feed composition and scattered separation results*. International Journal of Mineral Processing, 75, 189–196.

DRZYMALA J., AHMED H.A.M. (2005). *Mathematical equations for approximation of separation results using the Fuerstenau upgrading curves*. International Journal of Mineral Processing, 76(1-2), 55–65.

DRZYMALA J., KOWALCZUK P.B., OTENG-PEPRAH M., FOSZCZ D., MUSZER A., HENC T., LUSZCZKIEWICZ A. (2013). *Application of the grade-recovery curve in the batch flotation of Polish copper ore*. Minerals Engineering, 49, 17–23.

DRZYMALA J. (2006). *Atlas of upgrading curves used in separation and mineral science and technology*. Physicochemical Problems of Mineral Processing, 40, 19–29.

FINCH J., ZHANG W. (2014). *Frother function-structure relationship: Dependence of CCC95 on HLB and H-ratio*. Minerals Engineering, 61, 1–8.

GUPTA A.K., BANERJEE P.K., MISHRA A., SATISH P., PRADIP (2007). *Effect of alcohol and polyglycol ether frother on foam stability, bubble size and coal flotation*. International Journal of Mineral Processing, 82(3), 126–137.

HEYES G.W., TRAHAR W.J. (1976). *The natural floatability of chalcopyrite*. International Journal of Mineral Processing, 4, 317–344.

JIA R., HARRIS G.H., FUERSTENAU D.W. (2002). *Chemical reagents for enhanced coal flotation*. Coal Preparation, 123–149.

KHOSHDAST H., MIRSHEKARI S., ZAHAB-NAZOURI A. (2015). *A model for predicting dynamic frothability index value for dual-frother blends*. Journal of Mining & Environment, 6(1), 119–124.

KOWALCZUK P.B. (2013). *Determination of critical coalescence concentration and bubble size for surfactants used as flotation frothers*. Industrial & Engineering Chemistry Research, 52(33), 11752–11757.

KOWALCZUK P.B., BULUC B., SAHBAZ O., DRZYMALA J. (2014). *In search of an efficient frother for pre-flotation of carbonaceous shale from the Kupferschiefer stratiform copper ore*. Physicochemical Problems of Mineral Processing, 50(2), 835–840.

KOWALCZUK P.B., ZALESKA E., DANCZAK O. (2015). *Flotation of carbonaceous copper shale-quartz mixture with poly(ethylene glycol) alkyl ethers.* Transactions of Nonferrous Metals Society of China, 25(1), 314–318.

KOWALCZUK P.B., ZAWALA J., KOSIOR D., DRZYMALA J., MALYSA K., (2016). *Three-phase contact formation and flotation of highly hydrophobic polytetrafluoroethylene in the presence of increased dose of frothers*. Ind. Eng. Chem. Res. 55(3), 839–843.

LASKOWSKI J.S., TLHONE T., WILLIAMS P., DING K. (2003). *Fundamental properties of the polyoxypropylene alkyl ether flotation frothers*. International Journal of Mineral Processing, 72, 289–299.

LASKOWSKI J.S. (2004). *Testing flotation frothers*. Physicochemical Problems of Mineral Processing, 38, 13–22.

MALYSA E., MALYSA K., CZARNECKI J. (1987). *A method of comparison of the frothing and collecting properties of frothers*. Colloids and Surfaces, 23, 29–39.

MELO F., LASKOWSKI J.S. (2006). *Fundamental properties of flotation frothers and their effect on flotation*. Minerals Engineering, 19(6-8), 766–773.

MILLER J.D., LIN C.-L., HUPKA L., AL-WAKEEL M.I. (2009). *Liberation-limited grade/recovery curves from X-ray micro CT analysis of feed material for the evaluation of separation efficiency*. International Journal of Mineral Processing, 93(1), 48–53.

NEETHLING S.J., CILLIERS J.J. (2008). *Predicting and correcting grade-recovery curves: theoretical aspects*. International Journal of Mineral Processing, 89(1–4), 17–22.

ZHANG W., NESSET J.E., RAO R., FINCH J.A. (2012). *Characterizing frothers through critical coalescence concentration (CCC)95-hydrophile-lipophile balance (HLB) relationship*. Minerals, 2, 208–227.