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IN SEARCH OF AN EFFICIENT FROTHER FOR PRE-FLOTATION OF CARBONACEOUS SHALE FROM THE KUPFERSCHIEFER STRATIFORM COPPER ORE

Przemysław B. KOWALCZUK^{*}, Batuhan BULUC^{**}, Oktay SAHBAZ^{**},
Jan DRZYMALA^{*}

^{*} Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
przemyslaw.kowalczuk@pwr.edu.pl

^{**} Department of Mining Engineering, Dumlupınar University, Kutahya, Turkey

Abstract: This paper shows that frothers such as aliphatic alcohols ($C_nH_{2n+1}OH$), poly(propylene glycols) ($HO(C_3H_6O)_mH$), poly(propylene glycol) alkyl ethers ($C_nH_{2n+1}O(C_3H_6O)_mH$) and poly(ethylene glycol) alkyl ethers ($C_nH_{2n+1}O(C_2H_4O)_mH$), can be used for collectorless flotation of a sample of carbonaceous copper shale manually separated from the Kupferschiefer stratiform copper ore. It was shown that flotation is influenced by the type and dose of frothers. The best flotation results were obtained with tri(propylene glycol) butyl ether C_4P_3 , tri(propylene glycol) propyl ether C_3P_3 and tri(propylene glycol) P_3 . For these frothers, the yield vs. frother dose relationship was in the form of convex curves indicating that carbonaceous copper shale can float at relatively low dosages of the frother. It means that these frothers can be used for pre-flotation of carbonaceous matter from the investigated copper ore. Other frothers formed concave yield–frother dose relationships and were less effective.

Keywords: *frother, pre-flotation, copper ore, shale*

Introduction

Frothers play a very important role in mineral processing. They reduce bubble size, prevent bubble coalescence and stabilize the froth (Cho and Laskowski, 2002). The influence of the type and dose of frothers on the flotation performance has been studied by many authors (Malysa et al., 1987; Laskowski, 2001; Pugh et al., 2007; Drzymala et al., 2007; Kowalczuk et al., 2014). Konieczny et al. (2013) showed that a mixture of frothers from the poly(ethylene glycol) alkyl ethers family, even applied without any collector, can be used to float carbonaceous shale from the Kupferschiefer stratiform copper ore located in Poland. Therefore, frothers alone can be applied for a

partial separation of organic carbon from the copper ore during the so-called pre-flotation (Konieczny et al., 2013). The pre-flotation stage is designed to reduce the amount of carbon in the final copper concentrate to make it suitable for a further pyrometallurgical processing. The removal of organic carbon from the copper concentrates is also very important because the presence of shale significantly decreases the copper content in the final concentrates (Foszcz and Drzymala, 2011). Konieczny et al. (2013) showed that pre-flotation of carbonaceous matter from the copper ore is possible, however they used only one industrial frother. In this work, we investigate the influence of the type and dose of eleven different frothers on flotation of carbonaceous copper shale originated from the Kupferschiefer stratiform copper deposit mined by KGHM Polska Miedz S.A.

Experimental

Flotation tests with carbonaceous copper shale were carried out in a Mekhanobr laboratory flotation machine. A sample of carbonaceous copper shale originated from the Kupferschiefer stratiform copper deposit (Fore-Sudetic Monocline copper ore) located in SW Poland. The advancing and receding contact angles for the investigated shale/water/air system was 42° and 24°, respectively (Bednarek, 2014). Seventy grams of the sample and distilled water were mixed together and agitated for two minutes in a 0.25 dm³ flotation cell before adding any reagents. In each flotation tests the air flow rate was 20 dm³/min and the stirring speed was 1200 rpm. The experiments were carried out under natural pH. The samples of carbonaceous copper shale were floated in the presence of different aliphatic alcohols (C_nH_{2n+1}OH), poly(propylene glycols) (HO(C₃H₆O)_mH), poly(propylene glycol) alkyl ethers (C_nH_{2n+1}O(C₃H₆O)_mH) and poly(ethylene glycol) alkyl ethers (C_nH_{2n+1}O(C₂H₄O)_mH) at three different concentrations of 0.044, 0.086, and 0.136 mmol/dm³. The total time of flotation was 7 minutes in each test. The flotation products, that is concentrates and tailings, were dried and weighted to determine the concentrate yield.

The chemical reagents were obtained from Sigma-Aldrich (≥98% pure) and were used without further purification. The properties of the used chemical reagents, that is hydrophilic-lipophilic balance (HLB), molecular weight (MW), and critical coalescence concentration are given in Table 1. The value of the hydrophilic-lipophilic balance depends on hydrophilic and lipophilic (hydrophobic) groups in the considered molecule and can be estimated using formula $HLB = 7 + 1.3 \cdot (O) + 1.9 \cdot (OH) - 0.475 \cdot (C_xH_y)$ (Davies, 1957), where O and OH are numbers of hydrophilic oxygen and hydroxyl functional groups, respectively, and C_xH_y stands for the numbers of lipophilic (hydrophobic) –CH, –CH₂–, CH₃–, =CH– groups. The critical coalescence concentration (CCC₉₅), which characterizes reagent ability to prevent bubble coalescence, was calculated basing on the chemical structure of the frother, that is its molecular weight (MW) and hydrophilic-lipophilic balance (HLB), using a formula proposed by (Kowalczyk, 2013):

$$CCC_{95} = \frac{209.71 \cdot (HLB/MW)}{105.14 - 800(HLB/MW)} \quad (1)$$

The CCC_{95} indicates the frother concentration at which there is a ninety five per cent reduction in the Sauter mean bubble diameter in comparison to the Sauter mean bubble diameter in water only (Zhang et al., 2012).

Table 1. Properties of chemical reagents used in flotation of carbonaceous copper shale
(n indicates number of carbon atoms in the alkyl groups while m stands for number of glycolic groups)

Type	n	m	HLB	MW g/mol	CCC_{95} mmol/dm ³
Aliphatic alcohols (C _n H _{2n+1} OH, C _n)					
1-Hexanol, C ₆ H ₁₃ OH	6	0	6.05	102	0.215
1-Nonanol, C ₉ H ₁₉ OH	9	0	4.63	144	0.085
1-Undecanol, C ₁₁ H ₂₃ OH	11	0	3.68	172	0.051
Poly(propylene glycols) (HO(C ₃ H ₆ O) _m H, P _m)					
Tri(propylene glycol), HO(C ₃ H ₆ O) ₃ H	0	3	9.13	192	0.149
Poly(propylene glycol) alkyl ethers (C _n H _{2n+1} O(C ₃ H ₆ O) _m H, C _n P _m)					
Tri(propylene glycol) methyl ether, C ₁ H ₅ O(C ₃ H ₆ O) ₃ H	1	3	7.98	206	0.110
Tri(propylene glycol) propyl ether, C ₃ H ₇ O(C ₃ H ₆ O) ₃ H	3	3	7.03	234	0.078
Tri(propylene glycol) butyl ether, C ₄ H ₉ O(C ₃ H ₆ O) ₃ H	4	3	6.55	248	0.066
Poly(ethylene glycol) alkyl ethers (C _n H _{2n+1} O(C ₂ H ₄ O) _m H, C _n E _m)					
Ethylene glycol monobutyl ether, C ₄ H ₉ O(C ₂ H ₄ O) ₁ H	4	1	7.35	118	0.236
Di(ethylene glycol) monoethyl ether, C ₂ H ₅ O(C ₂ H ₄ O) ₂ H	2	2	8.65	134	0.252
Di(ethylene glycol) monohexyl ether, C ₆ H ₁₃ O(C ₂ H ₄ O) ₂ H	6	2	6.75	190	0.097
Tri(ethylene glycol) monobutyl ether, C ₄ H ₉ O(C ₂ H ₄ O) ₃ H	4	3	8.05	206	0.111

Results and discussion

The influence of frother type and concentration on recovery of carbonaceous copper shale originated from the Kupferschiefer stratiform copper deposit was evaluated using eleven different frothers including aliphatic alcohols, poly(propylene glycols), poly(propylene glycol) alkyl ethers and poly(ethylene glycol) alkyl ethers. The flotation results are shown in the form of concentrate yield versus frother concentration expressed in three different forms, that is in mmol of frother per volume of solution (mmol/dm³) (Fig. 1a), mass of frother per volume of solution (g/dm³) as well as mass of frother per mass of shale (g/Mg) (Fig. 1b). In the case when the amount of solids and aqueous medium is the same, the g/dm³ and g/Mg concentrations are the same. The flotation results were plotted in three different forms since it is not obvious what should be the concentration base for comparison of flotation results when different frothers are used. According to Malysa et al. (1987) the most promising base is a product of dynamic foamability index and frother concentration (DFI-c), however this approach is still awaiting for a wider verification.

Regardless of the way of expressing the frother concentration, two effects can be seen from Figures 1a and 1b. The first one indicates that for all reagents the concentrate yield increases with frother concentration, meaning that all of the considered in this work frothers can be used for carbonaceous shale flotation. The second observation is that the frothers can be divided into two families. The first group, with a convex shape of the yield vs. frother concentration curves is formed by the poly(propylene glycol) alkyl ethers C_nP_m and poly(propylene glycols) P_m . They float well carbonaceous copper shale at a relatively low dosage of the frother. The second group consists of poly(ethylene glycol) alkyl ethers C_nE_m and aliphatic alcohols C_n . For the second group the high recovery of carbonaceous copper shale is possible only at high frother concentrations.

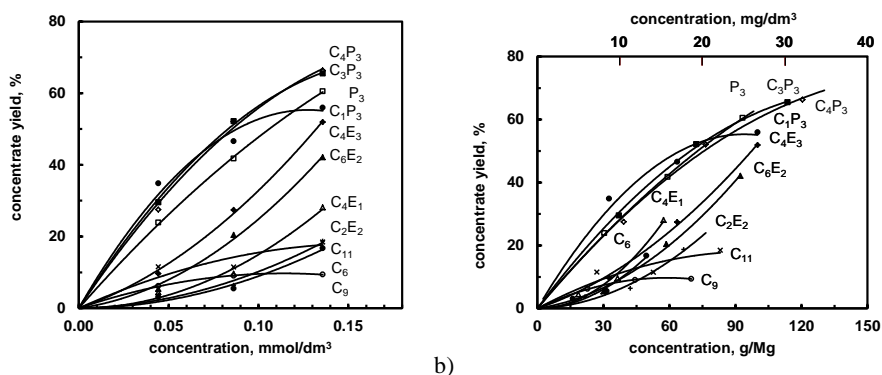


Fig. 1. Influence of frother concentration on shale concentrate yield, (a) concentration in mmol/dm^3 , and (b) in g/Mg and in mg/dm^3

The chemical structure of frother plays a role in flotation (Malysa et al., 1987; Harris and Jia, 2000; Laskowski, 2001; Drzymala et al., 2007; Kowalczyk et al., 2014). One of essential parameters of a frother is its critical coalescence concentration (CCC). This parameter indicates the frother concentration at which the bubble coalescence is prevented (Cho and Laskowski, 2002). To show the influence of the critical coalescence concentration on the recovery of carbonaceous copper shale, the data from Fig. 1 were re-plotted to show concentrate yield versus normalized frother concentration (C/CCC_{95}), where frother concentration C and critical coalescence concentration CCC_{95} are expressed in the same units.

Figure 2 confirms the observation resulting from Figs. 1, that the investigated frothers can be used for flotation of hydrophobic shale particles and there are two, convex and concave patterns of the flotation yield-concentration curve.

Figures 1 and 2 clearly show that the lowest recovery of the carbonaceous copper shale is obtained with the aliphatic alcohols. Only for 1-hexanol the recovery exceeds 20%. The low efficiency of 1-nonanol and 1-undecanol is probably caused by their very low solubility in water. On the other hand, the best results were obtained for poly(propylene glycols) and poly(propylene glycol) alkyl ethers. The recovery of the

carbonaceous copper shale exceeds 60% only with tri(propylene glycol) butyl ether C_4P_3 , tri(propylene glycol) propyl ether C_3P_3 and tri(propylene glycol) P_3 .

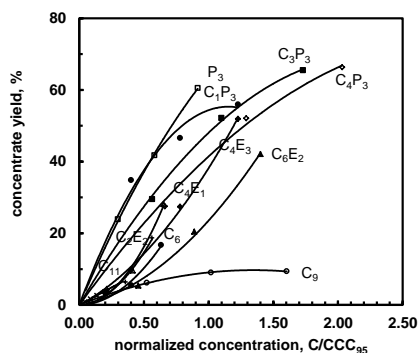


Fig. 2. Influence of normalized frother concentration C/CCC_{95} on concentrate yield

Among the investigated poly(ethylene glycol) alkyl ethers the best flotation occurs for the C_4E_3 and C_6E_2 frothers, while the yields for the remaining ethers, that is C_2E_2 , C_4E_1 , are very similar. However, it was shown elsewhere (Kowalczuk et al., 2014) that C_6E_2 and C_4E_1 exhibit an affinity towards quartz. Therefore, a low selectivity of copper ore flotation is expected in the presence of these frothers. Thus, poly(ethylene glycol) alkyl ethers with four carbon atoms in the alkyl (C_4) group and relatively high number (3) of ethylene groups provide high recovery of carbonaceous copper shale (Fig. 3a). Figures 1a and 1b also show that poly(propylene glycol) alkyl ethers C_nP_m form one, somehow scattered family of lines, exhibiting almost the same behaviour. However, the same results plotted as a 3D graph (Fig. 3b), indicate that from the C_nP_m family of frothers the most appropriate are those with four carbon atoms in the alkyl (C_4) group and having either three or four propylene (P_3 and P_4) groups.

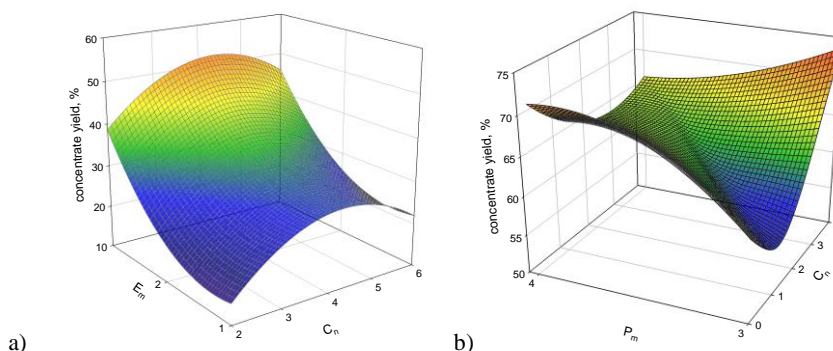


Fig. 3. Influence of number of carbon atoms in the alkyl (C_n) group, number of ethylene (E_m) (a) and propylene (P_m) (b) glycol groups in the chemical formula of frother on the concentrate yield for frother concentration equal to 0.136 mmol/dm^3

Conclusions

It appears from our investigations that all investigated frothers from the aliphatic alcohols, poly(propylene glycols), poly(propylene glycol) alkyl ethers and poly(ethylene glycol) alkyl ethers families can be used for pre-flotation of carbonaceous copper shale originated from the Kupferschiefer stratiform copper ore mined by KGHM Polska Miedz S.A. in the absence of any collector. The flotation performance depends on the frother type and dose. It was established that the yield versus frother concentration plots form two, convex and concave, patterns of the flotation curve. The best flotation results were obtained for C₄P₃, C₃P₃ and P₃. These frothers form the convex concentrate yield-frother dose relationship indicating that they float carbonaceous copper shale at a relatively low dosage of the frother.

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References

- CHO Y.S., LASKOWSKI J.S., 2002, *Effect of flotation frothers on bubble size and foam stability*, Int. J. Miner. Process., 64, 69–80.
- BEDNAREK P., 2014, *Contact angle of carbonaceous copper shale for different chemical reagents*. BSc Thesis, Wrocław University of Technology, in Polish.
- DAVIES J.T., 1957, *A quantitative kinetic theory of emulsion type, I. Physical chemistry of the emulsifying agent, Gas/liquid and liquid/liquid interface*. Proceedings of the International Congress of Surface Activity, 426–438.
- DRZYMALA J., MILCZARSKI E., MILCZARSKI J., 2007, *Adsorption and flotation of hydrophilic and hydrophobic materials in the presence of hydrocarbon polyethylene glycol ethers*, Colloids and Surfaces A: Physicochem. Eng. Aspects, 308(1–3), 111–117.
- FOSZCZ D., DRZYMALA J., 2011, *Differentiation of organic carbon, copper and other metals contents by segregating flotation of final Polish industrial copper concentrates in the presence of dextrin*, Physicochem. Probl. Miner. Process., 47, 17–26.
- HARRIS G.H., JIA R., 2000, *An improved class of flotation frothers*, Int. J. Miner. Process., 58(1–4), 35–43.
- KONIECZNY A., PAWLOS W., KRZEMINSKA M., KALETA R., KURZYDLO P., 2013, *Evaluation of organic carbon separation from copper ore by pre-flotation*, Physicochem. Probl. Miner. Process., 49(1), 189–201.
- KOWALCZYK P.B., 2013, *Determination of critical coalescence concentration and bubble size for surfactants used as flotation frothers*, Ind. Eng. Chem. Res., 52(33), 11752–11757.
- KOWALCZYK P.B., ZALESKA E., DANCZAK O., 2014, *Flotation of a model carbonaceous copper shale-quartz mixture with poly(ethylene glycol) alkyl ethers*, submitted to Transactions of Nonferrous Metals Society of China.
- LASKOWSKI J.S., 2001, *Coal flotation and fine coal utilization*, Vol. 14, in Developments in mineral processing, Elsevier Science Publishing, Amsterdam, The Netherlands.
- 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.
- PUGH R.J., 2000, *Non-ionic polyethylene oxide frothers in graphite flotation*, Miner. Eng., 13(2), 161–162.
- 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.