



## Flotation of carbonaceous copper shale–quartz mixture with poly(ethylene glycol) alkyl ethers



Przemyslaw B. KOWALCZUK, Emilia ZALESKA, Oliver DANCZAK

Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, Wroclaw 50-370, Poland

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**Abstract:** The influence of different poly(ethylene glycol) alkyl ethers ( $C_nH_{2n+1}O(C_2H_4O)_mH$ ,  $C_nE_m$ ) on flotation of carbonaceous copper shale mixed with quartz as a gangue mineral was investigated. The results show that all of the ethers  $C_4E_1$ ,  $C_4E_2$ ,  $C_4E_3$ ,  $C_2E_2$ ,  $C_6E_2$  investigated can be used for the flotation of carbonaceous copper shale. The best selectivity of separation in the flotation of the carbonaceous copper shale and quartz mixture is obtained with the  $C_4E_2$  and  $C_2E_2$  ethers. The obtained data can be used for developing separation of organic carbon present in carbonaceous shale at a rougher flotation stage on an industrial scale.

**Key words:** flotation; frother; selectivity; shale; quartz; poly(ethylene glycol) alkyl ethers

### 1 Introduction

Flotation is a physico-chemical process commonly used for upgrading of ores and other materials. This process is used to separate valuable materials from unwanted ones utilizing the differences of their surface properties. These properties can be modified using different chemical reagents. Since collectors are adsorbed at the solid/liquid interface, they are used to promote successful attachment of a valuable particle to a bubble and form a stable particle-bubble aggregate [1,2]. On the other hand, depressors are used to make the unwanted particles hydrophilic. While the collectors influence particle hydrophobicity, the role of frothers, which are adsorbed mainly at the liquid/gas interface, is to prevent the bubbles coalescence and stabilize the bubble attachment in the pulp froth layer, and therefore to enhance the efficiency of flotation process [3,4].

It is well established that the type, chemical structure and amount of reagent are very important in froth flotation providing different flotation recoveries of the solid particles [5–8]. The chemical reagents used as collectors can be characterized by hydrophobicity (contact angle) of solid particles, while frothers are mostly characterized by their relative molecular mass, hydrophilic-lipophilic balance (HLB), dynamic foamability index (DFI), critical coalescence

concentration (CCC) and reagent dosage (C) [3,9,10]. Some flotation frothers can act both as frothers and collectors when they are able to be adsorbed not only at the liquid/gas interface but also at solid/gas and solid/water interfaces, rendering the solid particles hydrophobic and floatable [11]. One group of such reagents exhibiting adsorption onto selected solid surfaces are poly(ethylene glycol) alkyl ethers ( $C_nH_{2n+1}O(C_2H_4O)_mH$ ,  $C_nE_m$ ), which are used for upgrading of different materials, including coal [12–14], graphite [15], quartz [16–18] and phosphate ores [19].

In this work, the influence of selected poly(ethylene glycol) alkyl ethers ( $C_nH_{2n+1}O(C_2H_4O)_mH$ ,  $C_nE_m$ ) on the flotation performance of a model mixture of carbonaceous copper shale and quartz as a gangue material was investigated. The experiments were performed to establish a better understanding of the role of  $C_nE_m$  ethers in froth flotation.

### 2 Experimental

Flotation tests were carried out in a Mekhanobr laboratory flotation machine equipped with a 0.25 L cell. A geological sample of carbonaceous copper shale was originated from the Kupferschiefer stratiform copper ore (Legnica-Glogow Zechstein Copper Basin LGOM), while quartz (98%  $SiO_2$ , 0.05%  $Fe_2O_3$ , 0.3%  $TiO_2$ ) was originated from the Osiecznica Mine, located in

southwestern Poland. Advancing and receding contact angles for the air/shale/water system were 42° and 24°, respectively. A 70 g of mixture of carbonaceous copper shale (10 g) and quartz (60 g), both with the narrow size fraction of 40–100 μm, and distilled water were mixed together and agitated for 2 min in the flotation cell before adding any reagent. In each test, the air flow rate was 10 L/h and the stirring speed was 1200 r/min. The experiments were performed under natural pH conditions. The samples were floated in the presence of different poly(ethylene glycol) alkyl ethers ( $C_nH_{2n+1}O(C_2H_4O)_mH$ ,  $C_nE_m$ ) at three concentrations equal to 0.028, 0.070 and 0.112 mmol/L. After the reagent addition, the pulp was conditioned for 5 min. The concentrates were collected after 1, 3 and 7 min as the froth products. The total time of flotation was 7 min in each test. The flotation products (froth products and tailing) were dried in an oven at 100 °C for 24 h and then weighed to determine the concentrate yield. Since carbonaceous copper shale (black) and quartz (white) varied in colour, their contents in the flotation products were determined using a Motic SFC-11 microscope.

The flotation reagents used in this work were obtained from Sigma-Aldrich (≥99% purity) and were used without further purification. Table 1 gives the properties of the poly(ethylene glycol) alkyl ethers ( $C_nH_{2n+1}O(C_2H_4O)_mH$ ,  $C_nE_m$ ) family including the numbers of alkyl ( $n$ ) and ethylene glycol ( $m$ ) groups, hydrophilic-lipophilic balance (HLB), relative molecular mass ( $M$ ) and critical coalescence concentration ( $CCC_{95}$ ).

The value of the hydrophilic-lipophilic (hydrophobic) balance depends on the number of hydrophilic and hydrophobic groups in the molecule and

can be calculated using a formula proposed by DAVIES [20]:  $HLB=7+1.3n(O)+1.9n(OH)-0.475n(C_xH_y)$ , where  $n(O)$  and  $n(OH)$  are the numbers of hydrophilic oxygen and hydroxyl functional groups, and  $n(C_xH_y)$  stands for the numbers of hydrophobic (lipophilic) —CH, —CH<sub>2</sub>—, —CH<sub>3</sub>—, and =CH— groups. Table 1 gives that higher numbers of lipophilic groups cause higher values of HLB. For all considered ethers in this work, the HLB values exceed 5.1, indicating that they all are frothers.

The critical coalescence concentration, expressed as  $CCC_{95}$ , characterizes the reagent ability to prevent the bubble coalescence [3]. The values of  $CCC_{95}$  are estimated based on the chemical structure of the frother, that is its relative molecular mass ( $M$ ) and hydrophilic-lipophilic balance [10]. The  $CCC_{95}$  indicates the frother concentration at which there is a 95% reduction in the mean bubble size in comparison to the mean bubble size in water only.

### 3 Results and discussion

The flotation tests were performed to investigate the influence of the type and dosage of selected poly(ethylene glycol) alkyl ethers on the flotation performance of a model mixture of carbonaceous copper shale and quartz. The results in the form of concentrate yield versus ether concentration are given in Fig. 1. It can be seen that three ethers, that is di(ethylene glycol) monohexyl  $C_6E_2$ , tri(ethylene glycol) monobutyl  $C_4E_3$  and mono(ethylene glycol) monobutyl  $C_4E_1$  follow a similar pattern and form one family of lines. Figure 1 shows that the concentrate yield increases with concentration expressed both in mmol/L and μg/g. The maximum yield value of 20% is obtained for  $C_6E_2$ . For di(ethylene glycol) monoethyl  $C_2E_2$  and di(ethylene glycol) monobutyl  $C_4E_2$  ethers, the concentrate yield remains almost constant and is equal to 10%. The results indicate that all the ethers investigated in this work improve the flotation up to a certain plateau level.

Figure 2(a) shows the influence of poly(ethylene glycol) alkyl ethers on the recovery of carbonaceous copper shale. It can be seen that all ethers form one family of lines and exhibit very high collecting properties of carbonaceous copper shale and the best results, exceeding 90% in recovery, are obtained for mono(ethylene glycol) monobutyl ether  $C_4E_1$ .

The influence of reagent concentration on the recovery of quartz, which is the gangue material, is shown in Fig. 2(a). Figure 2 indicates that three ethers, that is di(ethylene glycol) monohexyl  $C_6E_2$ , tri(ethylene glycol) monobutyl  $C_4E_3$  and mono(ethylene glycol) monobutyl  $C_4E_1$  ethers improve flotation of quartz and its recovery increases with concentration. For the other two

**Table 1** Properties of poly(ethylene glycol) ethers ( $C_nH_{2n+1}O(C_2H_4O)_mH$ ,  $C_nE_m$ )

Type	$n$	$m$	HLB	$M$	$CCC_{95}/$ (mmol·L <sup>-1</sup> )
Mono(ethylene glycol) monobutyl ether, $C_4H_9O(C_2H_4O)_1H$	4	1	7.35	118.17	0.236
Di(ethylene glycol) monoethyl ether, $C_2H_5O(C_2H_4O)_2H$	2	2	8.65	134.15	0.252
Di(ethylene glycol) monobutyl ether, $C_4H_9O(C_2H_4O)_2H$	4	2	7.70	162.23	0.148
Di(ethylene glycol) monohexyl ether, $C_6H_{13}O(C_2H_4O)_2H$	6	2	6.75	190.28	0.097
Tri(ethylene glycol) monobutyl ether, $C_4H_9O(C_2H_4O)_3H$	4	3	8.05	206.28	0.111

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