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ScienceDirect
Trans. Nonferrous Met. Soc. China 25(2015) 314−318
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

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

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Received 21 February 2014; accepted 7 June 2014

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

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DOI: 10.1016/S1003-6326(15)63606-8

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_2—, —CH_3—, 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.

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^{-1})
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

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

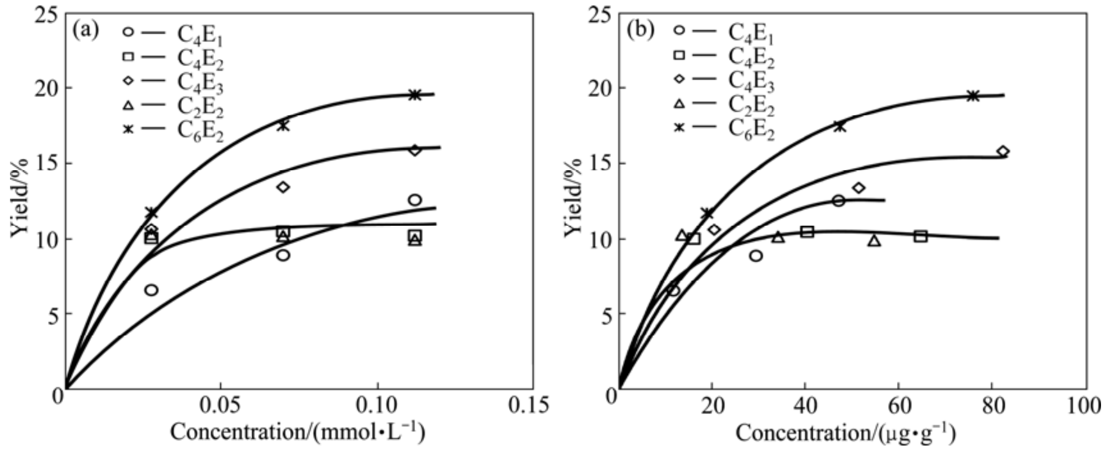

Fig. 1 Influence of ether concentration, expressed as mmol/L (a) and μg/g (b), on concentrate yield

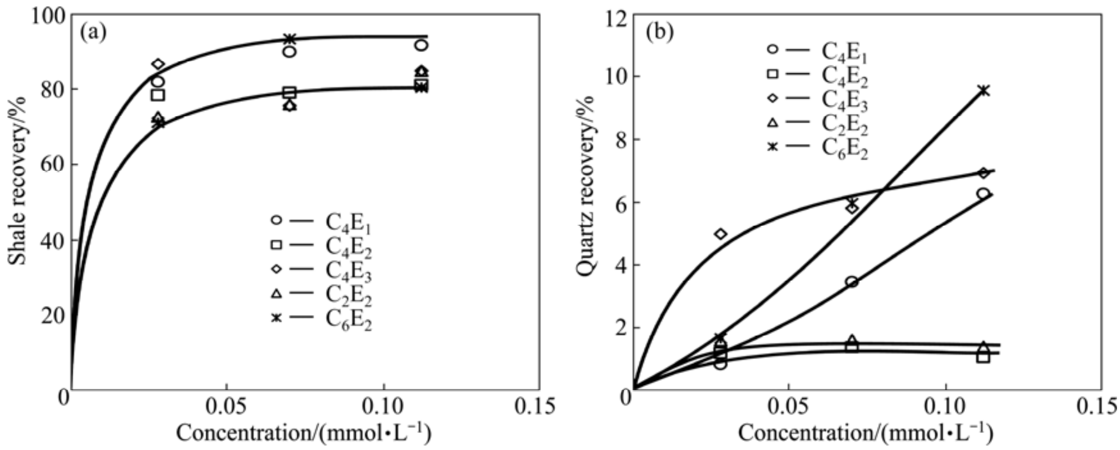

Fig. 2 Influence of ether concentration on recovery of shale (a) and quartz (b)

ethers, that is di(ethylene glycol) monoethyl C_2E_2 and di(ethylene glycol) monobutyl C_4E_2, the recovery of quartz is very low and remains constant with the reagent concentration. It means that among all ethers tested in this work, the latters can be used as selective ones during the flotation of materials consisting of quartz and carbonaceous copper shale.

To check the selectivity of flotation in the presence of the ethers, the results are plotted as a relationship between the recovery of shale in the concentrate and the recovery of quartz in the tailing. Such a relationship is also known as the Fuerstenau upgrading curve [21]. The upgrading curve for C_4E_3, as an example, is given in Fig. 3, where the solid points show the experimental data for the used concentration of 0.028, 0.070 and 0.112 mmol/L, respectively. The best approximation of the experimental points is obtained by using a nonlinear last-squares regression for one-adjustable parameter, called selectivity A, and has the form [22]:

$$A=\left(\frac{\varepsilon_{\mathrm{q,t}}+\varepsilon_{\mathrm{s,c}}-100}{\varepsilon_{\mathrm{q,t}}\cdot\varepsilon_{\mathrm{s,c}}}\right)\cdot 100 \tag{1}$$

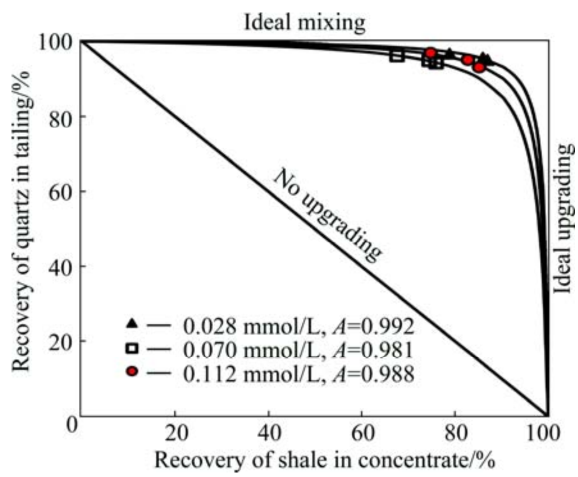

Fig. 3 Recovery of quartz in tailing versus recovery of carbonaceous copper shale in concentrate

where $\varepsilon_{\mathrm{q,t}}$ is the recovery of quartz in the tailing and $\varepsilon_{\mathrm{s,c}}$ is the recovery of shale in the concentrate. Selectivity A assumes values from 0 for non-selective flotation to 1 for an ideal upgrading process. Equation (1) and the Fuerstenau plot can be used to check the selectivity of any reagent used in flotation.

The selectivity of ethers in flotation of the mixture of carbonaceous copper shale and quartz is shown in Fig. 4 as a function of concentration expressed in mmol/L (Fig. 4(a)) and μg/g (Fig. 4(b)). It can be seen that the selectivity decreases with increasing frother dosage for C_4E_1, C_4E_3 and C_6E_2 and increases for C_2E_2 and remains constant or slightly increases for C_4E_2. It confirms that the used ethers form two groups of reagents. One of them is a group of the C_4E_1, C_4E_3 and C_6E_2 ethers, which provide the best selectivity of separation between shale and quartz, especially at low concentrations. Incidentally, C_4E_3 and C_6E_2 have relatively low values of the critical coalescence concentration CCC_{95} (Table 1). The second group is formed by the C_4E_2 and C_2E_2 ethers, for which the highest values of selectivity index A are obtained for relatively high values of ether concentration.

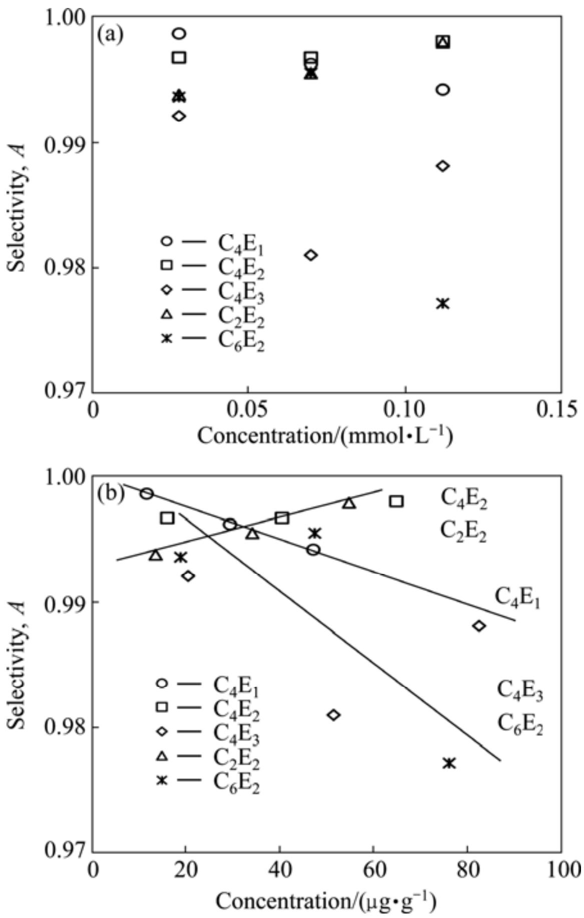

Fig. 4 Influence of ether concentration on selectivity of carbonaceous copper shale and quartz mixture expressed in mmol/L (a) and μg/g (b)

The influence of quartz recovery on the selectivity of flotation of the carbonaceous copper shale and quartz mixture is given in Fig. 5. It can be seen in Fig. 5 that the selectivity decreases with quartz recovery in the concentrate for all frothers at the used concentrations of frothers equal to 0.028, 0.070 and 0.112 mmol/L.

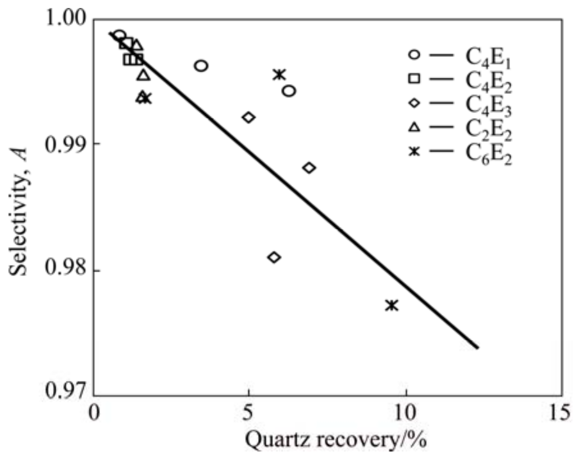

Fig. 5 Selectivity versus quartz recovery in concentrate

4 Conclusions

The influence of the type and dosage of poly(ethylene glycol) alkyl ethers on the flotation performance of model mixtures of carbonaceous copper shale and quartz was investigated. The results clearly show that all the used ethers, that is mono(ethylene glycol) monobutyl C_4E_1, di(ethylene glycol) monoethyl C_2E_2, di(ethylene glycol) monobutyl C_4E_2, di(ethylene glycol) monohexyl C_6E_2, tri(ethylene glycol) monobutyl C_4E_3 can be used for separation of carbonaceous copper shale from quartz by flotation. It is also established that the highest recoveries of quartz are obtained for C_4E_1, C_4E_3 and C_6E_2 ethers. The best selectivity of flotation of the carbonaceous copper shale and quartz mixture is observed for C_4E_2 and C_2E_2 ethers, which do not enhance quartz flotation. The obtained results can be used, for instance, to develop a technology for separation of organic carbon present in carbonaceous shale.

Acknowledgements

The authors thank Prof. Andrzej LUSZCZKIEWICZ (Wroclaw University of Technology) for his help in many aspects of this work. Financial support by the National Science Centre Research Grant (2012/07/D/ST8/02622) and a fellowships financed by the Foundation for Polish Science (FNP) and the European Union within the European Social Fund are also greatly acknowledged.

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碳质铜页岩−石英混合物的聚(乙二醇)烷基醚浮选

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摘　要：研究不同聚(乙二醇)烷基醚($C_nH_{2n+1}O(C_2H_4O)_m$, C_nE_m))对碳质铜页岩−石英混合物浮选的影响。研究结果表明：所研究的聚(乙二醇)烷基醚(C_4E_1，C_4E_2，C_4E_3，C_2E_2，C_6E_2)都可以作为碳质铜页岩的浮选剂。C_4E_2 和 C_2E_2 在碳质铜页岩和石英混合物的分离浮选过程中具有最佳的选出率。研究结果可为工业初选阶段分离碳质铜页岩中的有机碳提供参考。

关键词：浮选；起泡剂；选出率；页岩；石英；聚(乙二醇)烷基醚

(Edited by Yun-bin HE)