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Flotation of components of Polish copper ores using n–dodecane as a collector

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Abstract. Investigations on influence of aqueous emulsion of n–dodecane on flotation of sulfides and organic–carbon–containing shale from Legnica–Głogów Copper Basin (LGOM, Poland) are presented in the paper. Seven flotation experiments were conducted. Each flotation feed consisted of dolomite, quartz and one of following components: chalcopyrite, chalcocite, bornite, covellite, galena and shale containing organic carbon. The results indicate that chalcopyrite, bornite, covellite and shale float well in the presence of 200 g/Mg of n–dodecane and in a short period of time. Chalcocite and galena do not float with n–dodecane, even when the dose of the nonpolar collector for chalcocite flotation is increased. The studies explain a selective influence of the nonpolar collector on flotation of the copper sulfides ore from LGOM.

keywords: flotation, nonpolar collectors, sulfides, shale, chalcopyrite, chalcocite, bornite, covellite, galena

1. Introduction

Various sulfides are present in copper ores occurring in the Fore–Sudetic Monocline of SW Poland. According to Piestrzynski (2007) and Kucha (2007) the main copper sulfides are chalcocite, bornite, digenite, chalcopyrite, djurleite, covellite, spioncopite, geerite, yarrowite, tennantite and anilite. They are the source of copper produced from the concentrates of the flotation process. The collectorless and standard collector flotation of copper minerals originated from the Fore–Sudetic Monocline have been investigated by many investigators including Drzymala et al. (1993), Drzymala and Bigosinski (1995), and Lekki (1996, 1997, 2006). Typical collectors used for sulfide minerals flotation are xanthates (dithiocarbonates) and aerofloats (ditiophosphates) because they provide good separation (Gaudin, 1963; Bulatovic, 2007; Fuerstenau, 2007). However, the use of nonpolar reagents (oils) for copper sulfides flotation has not been investigated extensively.

Nonpolar reagents can be used in flotation of naturally hydrophobic minerals such as coal, graphite, sulfur, molybdenum, talc and mica (Seitz and Kawatra, 1986;

Vidlář and Pasiowiec, 2009). Literature on sulfides flotation indicates that complex hydrocarbons mixtures, like kerosene, fuel, engine, and plant oils (Nowakowska and Janicka, 1975; Seitz and Kawatra, 1986; Bos and Quast, 2000; Kondraty'ev and Izotov, 2000; Krausz et al., 2005; Rubio et al., 2007; Drzymala et al., 2008) can be used for flotation. This group of reagents plays many roles in flotation. These roles include (Seitz and Kawatra, 1986; Rubio et al., 2007; Drzymala et al., 2008) improving or inducing hydrophobicity of particles, reducing overall reagent costs by replacing part of the standard collector addition (nonpolar oils are less expensive reagents), improving selectivity of process, and increasing recovery of coarse and fine particles without reducing selectivity.

The nonpolar reagents are not soluble in water. It results in different mode of interaction with sulfides than that of soluble reagents. Oils must be emulsified before their application in separation processes. The emulsification of oils is important also in other ores beneficiation methods including selective agglomeration, solvent extraction and waste water treatment (Finkelstein, 1979).

Introduction of nonpolar reagents to flotation circuits changes the mechanism of air bubble–particle aggregate formation. Oils, due to their insolubility and high hydrophobicity, affect the air bubble–particle–water system differently than water soluble flotation collectors. The main difference is related to the physical adhesion of nonpolar reagent to the particle surface (Laskowski, 1992) by the van der Waals forces. The mechanism by which the oil acts is based on coating either a weakly or strongly hydrophobic particle leading to an improved adhesion of the air bubble to the particle (Seitz and Kawatra, 1986). Kondraty'ev and Izotov (2000) showed that an addition of oil to flotation systems increases hydrophobicity of particles and reduces the time of interruption of the aqueous layer between the liquid and air bubble.

Nonpolar reagents such as hydrocarbons and their derivatives are used in flotation as collectors which the main function is selective hydrophobization of the surface of particle. Usually complex mixture of hydrocarbons (Nowakowska and Janicka, 1975; Seitz and Kawatra, 1986; Bos and Quast, 2000; Krausz et al., 2005; Luszczkiewicz et al., 2006; Rubio et al., 2007; Drzymala et al., 2002, 2008) as used as a collector for copper sulfide ore flotation. In most papers, when the complex nonpolar reagent including kerosene, fuel, plant oils was used, the results of upgrading were worse than those with standard copper ore flotation such as xanthates (Drzymala et al., 2002, 2008; Luszczkiewicz et al., 2006; Bakalarz, 2011). The authors of these studies suggested that probably only selected sulfides float in the presence of the nonpolar collectors. The remaining sulfides float only with xanthates. So far, it has not been determined which sulfides float well with the nonpolar collectors. The investigation on this aspect of sulfide flotation should explain the process of sulfide ore flotation in the presence of nonpolar collectors.

2. Experimental

2.1. Materials

Seven model ores were prepared. Each consisted of dolomite (47.5%, from Dolomite Mine in Libiaz, Poland), quartz (47.5%, from Osiecznica, Poland) and 5.0% of a given component (either chalcocite, bornite, chalcopyrite, covellite, galena or organic-carbon-containing shale from Polkowice-Sieroszowice or Rudna Mines, KGHM Polska Miedz S.A., Poland). Dolomite was wet ground in a laboratory ball mill (Alvarez Redondo) and next wet screened to get narrow size fractions of 40–71 micrometer used for the model feed. Quartz was only wet screened to get proper size fractions. Last component added to the model feed were prepared fresh daily by crushing manually in an agate mortar and dry screening to get the 40–71 micrometer size fraction. This procedure was dictated by the fact that microscopic analysis is accurate only for narrow size fractions of particles.

2.2. Reagents

n-dodecane (DD, 99%, Alfa Aestor) was used as a model nonpolar collector in all experiments. It was emulsified in distilled water directly before experiments in a laboratory whipper (POL-EKO Aparatura) for 8 minutes applying 18 000 rpm. The concentration of emulsion was 5 g/dm³. Methyl dipropylene glycol ether (C₁P₂, 97%, Aldrich) was used as a frother. The solution containing 3 g/dm³ of C₁P₂ was prepared in distilled water. In each experiment the dose of frother was 200 g/Mg.

2.3. Methods

Seven flotation experiments were conducted. In six flotation tests with either chalcocite, bornite, chalcopyrite, covellite, galena or shale the aqueous emulsion of n-dodecane (DD) was used as the collector in the amount of 200 g/Mg. Additionally, one more experiment with chalcocite was conducted in the presence of 400 g/Mg of n-dodecane. The flotation tests were conducted in a Mechanobr laboratory flotation machine (IMN Gliwice) equipped with 250 cm³ flotation cell, which was made from stainless steel. The mass of each feed was 70 g. The speed of stirrer was 760 min⁻¹ (rpm) and the flow of air 30 dm³/h.

Each feed sample was stirred with distilled water for 3 minutes. Next, the collector was added and the suspension was agitated for further 5 minutes. After that, frother was added and the suspension stirred for 1 minute. Next, the air valve was opened and the flotation initiated. The flotation concentrates were collected for about 10 minutes. All the flotation products were dried in a laboratory drier at 80°C and next weighted.

The samples for microscopic analysis were prepared using Canadian balm. A monolayer of particles in the balm was analyzed with a microscopic digital color camera (Nikon DS-Fi1-U2) and the Nikon NIS Elements BR software. The assay of

sulfide/shale was estimated in all flotations products by measurement the surface area of all particles.

The results of the experiments are presented as kinetic and upgrading separation curves known as the Halbich, Luszczykiewicz and Fuerstenau plots, which were described in details by Drzymala (2006–8).

3. Results and discussion

The results of investigations are presented in Figs. 1–4. The solid lines in Fig. 1 indicate kinetics (recovery of material vs. flotation time) of all flotation experiments. Around the first five minutes of flotation, a high recovery of the four materials was observed with the exception of galena and chalcocite, despite the fact that dose of n-dodecane for chalcocite flotation was increased. It can be also seen that chalcopyrite was the fastest floating component.

Flotation upgrading curves are presented in Figs. 2–4. It is assumed that chalcopyrite flotation is the most efficient since its upgrading curve lies very close to the ideal upgrading line shown in Fig. 2. Worse results were obtained for bornite, covellite and shale. It can be also seen that galena and chalcocite do not float when aqueous emulsion of n-dodecane is used as the collector, even if the dose of n-dodecane was increased from 200 to 400 g/Mg for chalcocite flotation. Three upgrading curves, both for chalcocite and one for shale lie almost on the “no upgrading” line. The next figure (Fig. 3), known as the Luszczykiewicz upgrading curve, shows similar situation. The closest curve to the ideal separation lines was obtained for chalcopyrite.

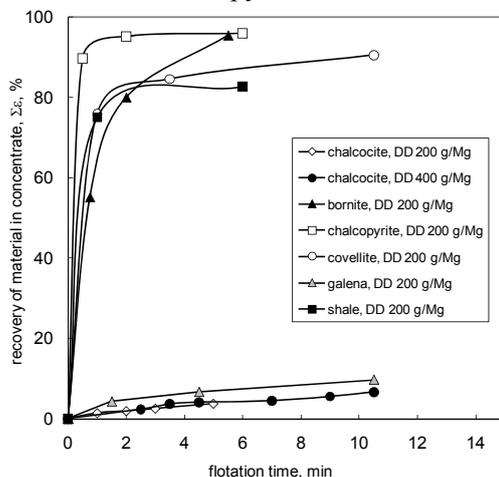


Fig. 1. Comparison of kinetic curves for all flotation experiments

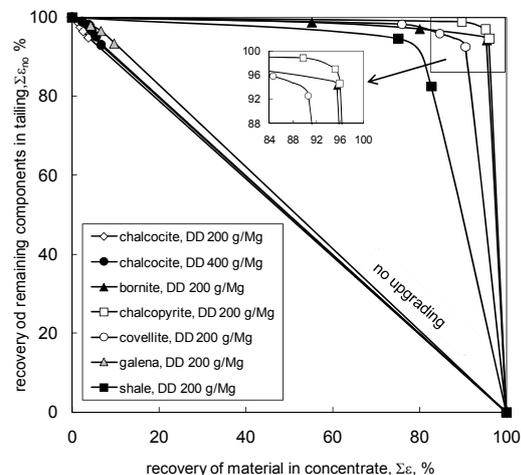


Fig. 2. Upgrading Fuerstenau's curves as recovery of remaining components in tailing vs. recovery of considered component in concentrate for all flotation experiments

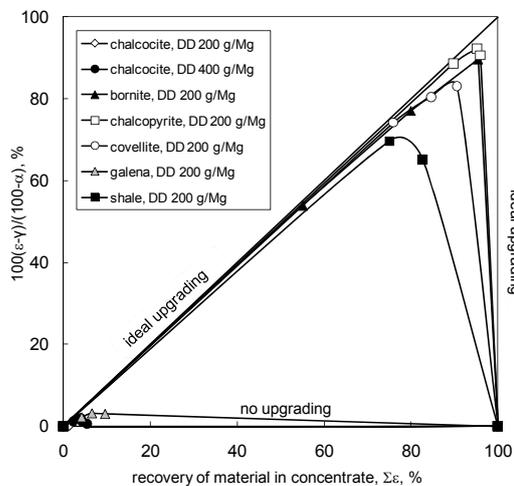


Fig. 3. Upgrading Luszczkiewicz's curves as a relationship between $100(\varepsilon-\gamma)/(100-\alpha)$ reflecting a component content in concentrate and recovery of the considered component in concentrate for all flotation experiments (γ , concentrate yield; ε , recovery in concentrate; α , content in feed)

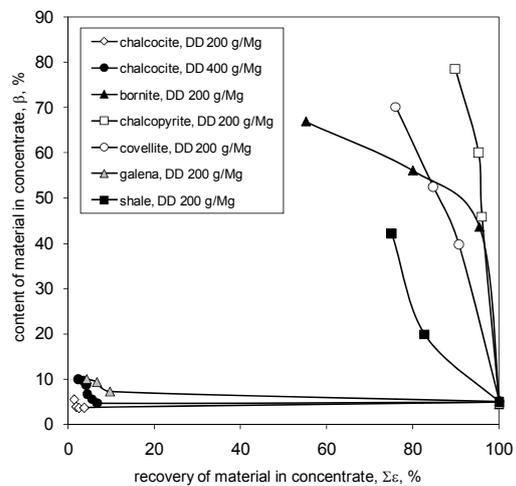


Fig. 4. Upgrading Halbich's curves as a relationship between component content in concentrate and recovery of the considered component in concentrate for all flotation experiments

Figure 4 shows, that the richest first concentrate was obtained during chalcopyrite flotation. The content of copper sulfide was around 80% at the recovery of about 90%. According to Figs. 2–4, not all covellite and organic-carbon-containing shale are recovered during flotation with *n*-dodecane. Probably, to float the rest of covellite an addition of a standard collector, such as xanthate to the flotation suspension would be necessary.

4. Conclusions

The effect of nonpolar collector on flotation of the main sulfides minerals and organic-carbon-containing shale from Legnica-Glogow Copper Basin has been investigated in the paper. The flotation of five minerals (chalcocite, bornite, chalcopyrite, covellite and galena) and organic-carbon-containing shale in the presence of *n*-dodecane has been studied. Results of the work indicate that chalcopyrite, bornite, covellite and shale float in the presence of *n*-dodecane as a collector. The time of their flotation was short, equal to about 2–10 minutes. The best results were obtained for chalcopyrite flotation. Chalcocite and galena do not float with *n*-dodecane and to float all covellite particles, probably an addition of one of the standard sulfide minerals collectors (xanthates or aerofloats) is necessary.

The obtained results explain the process of Polish copper sulfide ore flotation with nonpolar reagents. Presumably, the main reason of worse results of copper upgrading is that chalcocite or other copper sulfides which have not been examined in

the paper, do not float in the presence of oils. High recovery of the rest of examined copper minerals points to positive effect of the nonpolar collector. Good floatability of organic-carbon-containing shale in the flotation using n-dodecane explains high recovery of organic carbon in copper sulfide ore flotation. All the results suggest that the nonpolar collector can be used as an effective collector of sulfide minerals from LGOM, if combined with one of the standard collectors of sulfides, for instance xanthates. Additional detailed investigations on the natural copper ore, coupled with mineralogical characterization, should confirm selectivity of flotation using nonpolar reagents. This subject should be further investigated.

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W pracy przedstawiono wyniki flotacji głównych minerałów siarczkowych oraz łupka pochodzących z rejonu Legnicko-Głogowskiego Okręgu Miedziowego w obecności apolarnego odczynnika zbierającego. Zbadano wpływ wodnej emulsji n-dodekanu na flotowalność kolejno: chalkozynu, chalkopiryty, covellinu, bornitu, galeny oraz łupka w mieszaninie z dolomitem oraz kwarcem. Badania przeprowadzono dla wąskiej klasy ziarnowej 40–71 μm , a zawartość poszczególnych minerałów w produktach flotacji oznaczano mikroskopowo przy użyciu specjalistycznego oprogramowania. W obecności n-dodekanu w ilości 200 g/Mg zaobserwowano flotację chalkopiryty, bornitu, covellinu oraz łupka. Galena oraz chalkozyn nie uległy procesowi flotacji. Według dotychczas opublikowanych wyników badań flotacji siarczkowych rud miedzi, stwierdzono, że tylko część nośników miedzi wykazuje flotowalność w obecności olejów. Prawdopodobnie, stwierdzony brak flotowalności chalkozynu, a być może także innych siarczków miedzi nieanalizowanych w pracy, jest przyczyną gorszych wskaźników wzbogacalności procesów flotacji rud miedzi w obecności olejów. Dobra flotowalność łupka, który jest nośnikiem węgla organicznego, potwierdza wysokie uzyski tego składnika w procesach flotacji krajowej rudy miedzi w obecności odczynnika apolarnego. Zagadnienie wymaga dalszych szczegółowych badań

słowa kluczowe: flotacja, apolarne odczynniki zbierające, siarczki, łupek, chalkopiryt, chalkozyn, covellin, bornit, galena