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COLLECTORLESS FLOTATION OF SULFIDES OCCURRING IN THE FORE-SUDETIC COPPER MINERALS DEPOSIT OF SW POLAND

Abstract. Utilizing the maximum size of particles floating in a monobubble Hallimond tube, the collectorless flotation and hydrophobicity of sulfides in air-saturated water at pH 6.5—6.9 and redox potential E_h = 0.530-0.560 mV were determined. It was established that the collectorless flotation and hydrophobicity, expressed as contact angle, were increasing in the following order: djurleite (2.2^0) ~ chalcocite (2.4^0) ~ covellite (3.7^0) < chalcopyrite (6.9^0) ~ galena (7.6^0) ~ djurleite-bornite (8.4^0)< bornite $(12^0—17^0)$. Bituminous shale, which co-exists with sulfide minerals, was classified as a hydrophilic material.

INTRODUCTION

Copper minerals deposit located in the Fore-Sudetic Monocline of SW Poland contains such sulfide minerals as chalcocite, djurleite, digenite, chalcopyrite, bornite, covellite, galena, pyrite, sphalerite, tenantite, and marcasite (Harańczyk, Jarosz 1973). The copper sulfides in the ore are a main source of copper which is produced from concentrates after upgrading the ore by flotation with xanthates (Laskowski 1969). The non-copper sulfides present in the ore and subsequently in the flotation concentrates are a source of other metals such as useful silver and environmentally harmful lead.

The results of xanthate flotation as well as the consumption of flotation reagents depend on the surface properties of sulfides (Buckley, Woods 1991) which in turn depend on the environment during the formation of the sulfides and processes taking place between the time of formation and mining as well as the time of mining and flotation (Gutierrez 1973). Among the surface properties, hydrophobicity and native flotation are of great importance. Unfortunately, the native flotation of sulfides from the Polish copper minerals deposit has not been studied extensively and the present

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work was undertaken to fill out this gap. The difficulty to obtain sufficiently large samples of pure sulfides as well as unavailability of precise methods for determining the native flotation of minerals are the reasons for very limited data on the hydrophobicity and collectorless flotation of sulfides from the Fore-Sudetic Monocline. These obstacles were finally overcome due to geologists working in the copper mines who collected suitable samples as well as due to appearance of flotometry (Drzymala, Lekki 1989; Drzymala 1994; Lekki, Drzymala 1990) capable to measure both flotation and hydrophobicity.

EXPERIMENTAL

Materials

The sulfide samples have been collected over years at different locations of the deposit, and therefore, the precise origin of the specimens are not well known. Bituminous shale, commonly occurring in the deposit, was taken from the Lubin Mine and included in the investigations. The identity and structure of sulfides were determined by the X-ray and other mineralogical analyses (Table 1). The density of the solids was determined with a picnometer using water as the suspending medium (Table 2).

TABLE 1

Characteristics of solids used in flotation test

No.	Solid	Structure (based on x-ray data)	Impurities
1.	chalcocite	α — chalcocite (low temp., romb.)	~4% quartz ~1% carbonates
2.	covellite	hexagonal covellite	~4% quartz ~1% chalcopyrite
3.	chalcopyrite	tetragonal chalcopyrite	~6% calcite <1% quartz
4.	galena	cubic galena	~2% quartz
5.	djurleite-bornite	tetragonal bornite (~40%) + monoclinic djurleite (~60%)	~7% (quartz and carbonates)
6.	bornite	tetragonal bornite	<1% quartz
7.	djurleite	monoclinic djurleite	34% (clay+carbonate) 6% quartz
8.	bituminous shale	—	17% carbonates, 8% quartz

TABLE 2

Characteristics of investigated sulfides and flotometric results

ρ — density of mineral; s — standard feed sample; D_{max} — maximum size of floating particle
θ_s — approximate contact angle (Eq.2); θ_d — detachment contact angle (Eq. 3); θ —
equilibrium contact angle (Eq. 4); L_H — mechanical carryover index calculated from Eq.5.
Measured density values were used for calculation of S/ρ_p, contact angles, and L.

Sample	General data			Single particle flotation			Multi-particle flotation	
	ρ_p (exp.)	ρ_p^{**}	s/ρ_p	D_{max}	$\theta_s \approx \theta_d$ (Eq.2)	θ (Eq.4)	D_{max}	L_H
	g/cm^3	g/cm^3	cm^3	mm	deg.	deg.	mm	cm
Djurleite	5.06	5.50—5.80	0.130	0.064	2.2	1.2	0.064	0.026
Chalcocite	5.41	5.50—5.80	0.120	0.065	2.4	1.2	0.065	0.029
Covellite	4.40	4.59—4.76	0.132	0.115	3.7	1.9	0.115	0.039
Chalcopyrite	4.04	4.10—4.30	0.129	0.230	6.9	3.6	0.230	0.070
Galena	7.35	7.58	0.149	0.175	7.6	4.0	0.175	0.111
Djurleite-bornite	4.98	—	0.120	0.244	8.4	4.5	0.180	0.072
Bornite	4.71	5.07	0.131	0.30—0.50	12—17	6.5—9.6	0.500	0.157
Bituminous shale	2.41	—	0.112	0.16	<5.7*	—	0.160	0.021

* Assumed as in multi-particle flotation.

** After CRC Handbook 1987.

For the flotation tests, the sulfide lumps were crushed in an agate mortar and separated into narrow size fractions by means of screening. To reduce the oxidation of freshly created surfaces, the time between crushing and flotation was less than 30 minutes. Both flotation of individual sulfide particles, to determine their hydrophobicity, and flotation of a collection of particles, to establish floatability of interacting particles, were carried out.

Multi-particle flotation

The tests were carried out in a monobubble Hallimond tube (Hallimond 1944) modified by Ewers (Sutherland, Wark 1955) and later improved by Lekki (1973) who calibrated the receiver of the tube for continuous measurement of the solids recovery as a function of time. A sketch of the monobubble Hallimond tube is given in Fig. 1. Each investigated sample was introduced into 120 cm^3 of water in a beaker and agitated for 10 minutes. Then, the mixture was transferred to the Hallimond tube and floated with air at a flow rate of 0.625 cm^3/s. The volume occupied by the solids in the Hallimond tube compartment before flotation was kept constant (0.2 cm^3). Therefore, the weight of the solids used for flotation, also referred to as the standard feed sample (s), depended on the applied material, but the ratio between the standard feed sample and solid density was almost constant (Table 2). The overall flotation time was 30 minutes. The tests were carried out in air-saturated water at 20 ± 2^0C for different narrow size fractions of each mineral at natural pH equal to 6.5—6.9 and natural redox potential E_h equal to 0.530—0.560 mV. The diameter of bubbles was 4 ± 1 mm.

Ten particles were selected from each needed for testing size fraction. All ten particles were equilibrated with the aqueous solution for ten minutes, and then, one particle and the solution were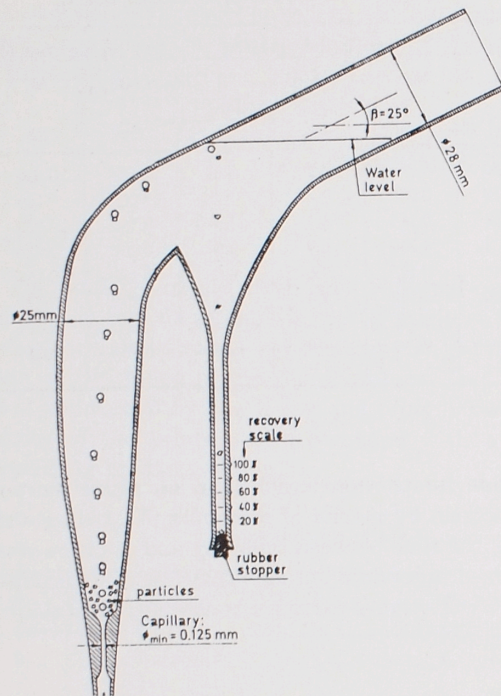 transferred to the Hallimond tube for flotation. If within 30 minutes of bubbling the air through the tube the particle was found in the calibrated receiver, it was counted as floatable. Subsequently, the particle was removed from the solution, and then a second particle was introduced for flotation. In this way all ten particles were subjected individually to flotation. The flotation recovery was calculated as the ratio of the number of floating particles to all 10 tested particles multiplied by 100%. The same procedure was repeated with another set of 10 particles or sometimes with a third set of 10 particles. The final recovery was calculated as an average recovery of all series. The flotation tests were carried out in air-saturated water at $20 \pm 2^0 C$ having natural pH equal to 6.5—6.9 and natural redox potential E_h equal to 0.530—0.560 mV.

Fig. 1. Monobubble Hallimond tube used in this study

RESULTS OF FLOTATION

Flotation tests provide relationships between recovery (R) and time of flotation (t). Such relationships for different size fractions of galena are shown in Fig. 2. It can be seen from part „a" of Fig. 2 that initially flotation recovery increases with the time of flotation and then levels off at a maximum constant value. This usually occurs, depending on the solid and its fraction size, between 10 and 20 minutes of flotation. Therefore, the recovery after 30 minutes of flotation is the maximum recovery (Rm) for a given solid floated in the Hallimond tube. The values of the maximum recovery for a given solid and different particle sizes can be used for drawing another relationship, i.e., maximum recovery (Rm) as a function of particle size (D). The recovery-size (Rm-D) plot is a variant of well
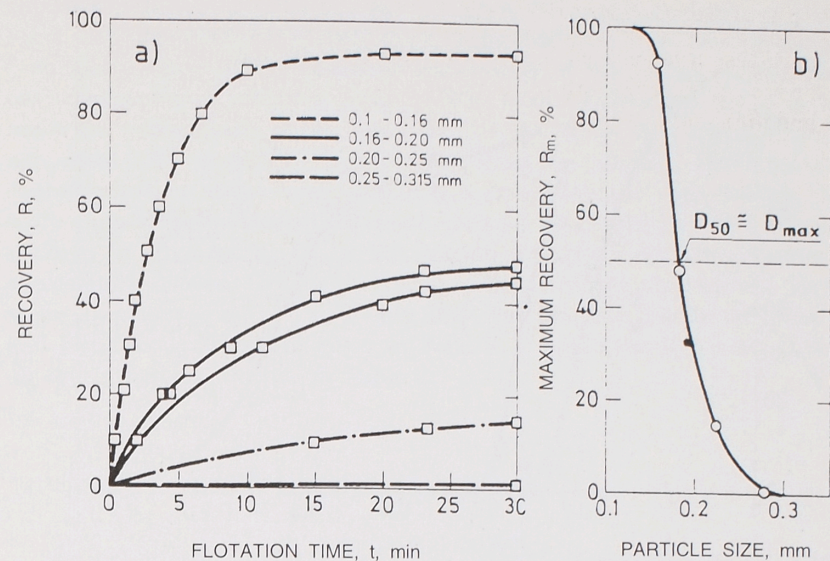

Fig. 2. Relationship between recovery and time of flotation for galena in monobubble Hallimond tube (a) and separation curve indicating maximum size of floating particles (b)
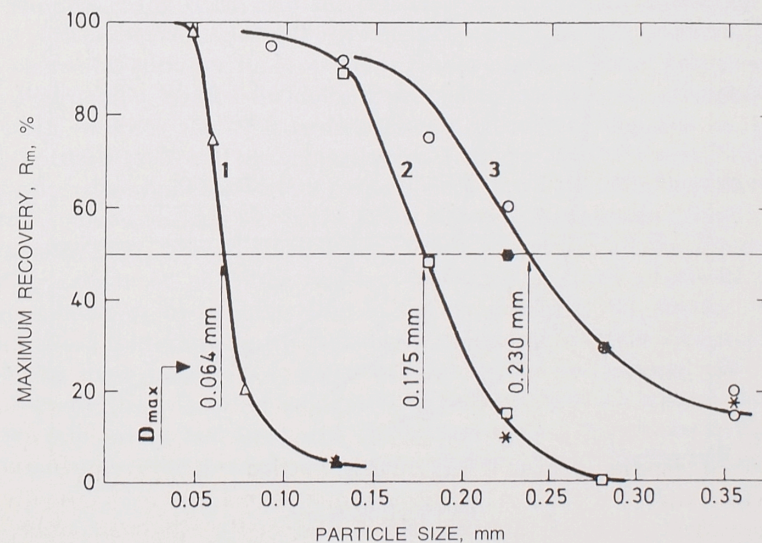

Fig. 3. Separation curves for djurleite (Δ), galena (□), and chalcopyrite (O). Symbol * denotes flotation of individual particles
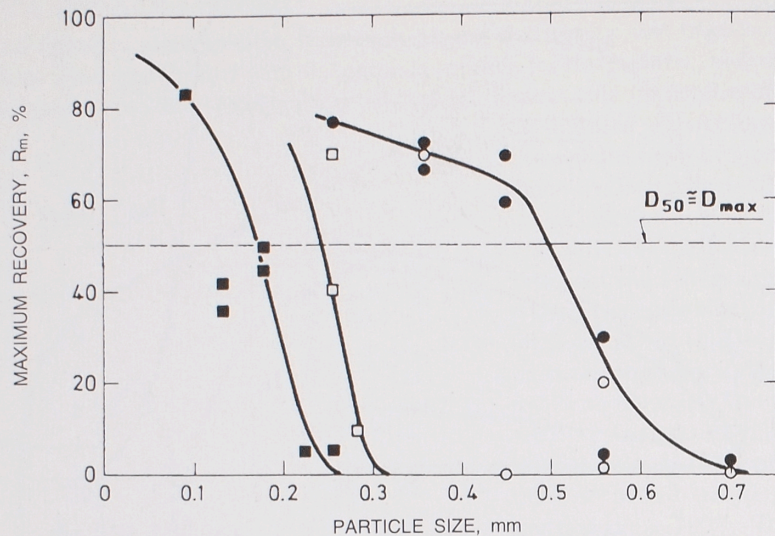
Fig. 4. Separation curves for djurleite-bornite (■, □) and bornite (O, ●). Open symbols denote flotation of individual particle. Filled symbols indicate flotation of a collection of particles
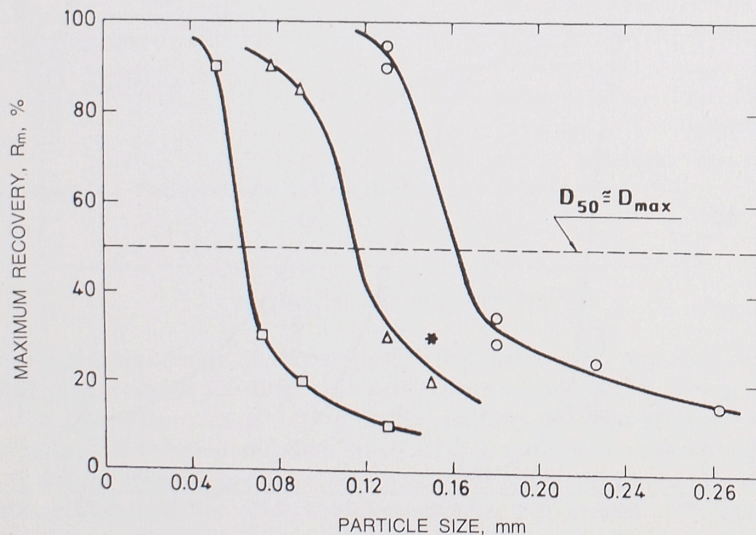

Fig. 5. Separation curves for chalcocite (□), covellite (△), and bituminous shale (O). Symbol * denotes flotation of individual particles of covellite

known separation or efficiency curve (Lynch 1977) and is shown as part „b" of Fig 2. The imperfect (not vertical), bell-shape character of the Rm -D curve results from fluctuations in the chemical composition of the grains, variations in the particles geometry within a given fraction used for flotation, and also from the imperfect performance of the separating device. When the separation curves are not ideal the so-called classification size D_{50} (Lynch 1977) is used for characterization of the whole separation curve, because each particle having a size equal to D_{50} possesses the same odds for successful flotation as well as for sinking. In other words D_{50} is the maximum particle size (D_{max}) which can be successfully floated, though the recovery of the whole size fraction having the mean diameter equal to D_{50} is only 50%. The flotation results for other sulfides and bituminous shale are given in Figs. 3—5 while the $D_{50} \approx D_{max}$ values for all the investigated solids in Table 2.

DISCUSSION

The list of most important naturally hydrophobic minerals is well known and consists of talc, sulfur, graphite, diamond, certain sulfides such as molibdenite and realgar (Gaudin et al. 1957). There is an uncertainty regarding the native hydrophobicity and collectorless flotation of sulfides of common metals. It results from the complexity of their chemistry as well as from the fact that the surface of sulfides easily react with the components air such as oxygen, water vapour, and carbon dioxide. Among the products of reactions are hydrophobic species such as elemental sulfur or its equivalents (sulfur excess sulfides, polysulfides) as well as hydrophilic species including hydroxides, oxides and carbonates. Different studies indicate that the hydrophobicity of sulfides depends on the amount (Richardson 1995) and the arrangements (Chander 1991) of the oxidation products. Investigations have shown that pyrite (Lekki, Drzymala 1990; Chmielewski, Nowak 1992), galena (Lekki, Drzymala 1990; Nowak, Chmielewski 1994), chalcopyrite (Chander 1991; Nowak, Chmielewski 1994), and other sulfides (Finkelstein et al. 1975; Arbiter et al. 1975) can be, depending on their oxidation path either hydrophobic or hydrophilic. Due to the complexity of the surface chemistry of sulfides, in this study the hydrophobicity and native flotation were studied without relating these properties to any particular species and process.

Usually, the measure of hydrophobicity is the angle which is formed at the contact of the solid, water, and air phases. This contact angle is determined by the interfacial free energies of the three phases involved and is given by the Young equation:

$$\sigma_{sa} = \sigma_{sw} + \sigma_{wa} \cos \theta \qquad (1)$$

where σ_{sa}, σ_{sw} and σ_{wa} are the free energy of the solid/air, solid/water, and water/air interfaces, respectively.

The contact angle for hydrophilic surfaces is equal to zero while for hydrophobic solids the contact angle is between zero and about 110° (Adamson 1982). The contact angle can be measured directly by placing a small drop of water on a flat and smooth surface. In the case when a large enough surface is unavailable the contact angle can be determined, for instance, from the maximum size of floating particle (D_{max}) and suitable equations relating contact angle with D_{max}. A simplified equation relating D_{max} with contact angle was offered by Scheludko and his co-workers (Scheludko et al. 1976):

$$\sin^2\left(\theta_s/2\right) = D_{max}^2\left(\rho_p - \rho_w\right)g/\left(6\,\sigma_{wa}\right) \qquad (2)$$

where g stands for acceleration due to gravity, ρ_p is the density of particle, ρ_w denotes the density of water, and θ_s is the approximate equilibrium contact angle. A more complete equation for calculating contact angle was derived by Schulze (1984) while Drzymala (1994) has shown that flotation tests can provide both the detachment (θ_d) and equilibrium (θ) contact angles which are given by the formulas:

$$0.5\pi D_{max}\,\sigma\left(1 - \cos\theta_d\right) - \left[1/6\,\pi D_{max}^3\,\rho_p\,g - 1/8\,\pi D_{max}^3\,\rho_w\,g\left\{2/3 + \cos\left(\theta_d/2\right) - 1/3\cos^3\left(\theta_d/2\right)\right\}\right] -$$

$$- 0.25\pi D_{max}^2\left(1 - \cos\theta\right)\left(\sigma/R - R\rho_w\,g\right) = 0 \qquad (3)$$

and

$$D_{max}/2\sin\left(\theta_d/2\right) = R\sin\left(\theta - \theta_d/2\right) \qquad (4)$$

where R is the radius of the bubble and π is equal to 3.14. It should be added that Eqs. 2—4 are valid for D_{max} obtained from quasistatic flotation tests in which no interaction between particles takes place. This requirement is nearly fulfilled in the flotation of individual particles in the monobubble Hallimond tube without stirring which was used in this work. The results of measurements of D_{max} from flotation of individual particles in the monobubble Hallimond tube and contact angles calculated from Eqs. 3—4 are presented in Table 2. The values of the contact angles indicate that sulfides from the Lubin-Głogów Copper Region are very weakly hydrophobic and their contact angles are small.

There is one more parameter which can distort the information on the hydrophobicity of solids determined from flotation tests. This parameter is the mechanical carryover of particles. It was established previously by testing a great number of hydrophilic substances that the mechanical carryover of particles with density above 2.0 g/cm^3 in the monobubble Hallimond tube is governed by the flotometric equation:

$$D_{max}\left(\rho_p - \rho_w\right)/\rho_w = L_H \qquad (5)$$

and the value of L_H is equal to 0.023 ± 0.002 cm. For less dense solids the flotometric equation becomes:

$$D_{max}\left\{\left(\rho_p - \rho_w\right)/\rho_w\right\}^{0.75} = L_L \qquad (6)$$

and L_L value is equal to 0.020 ± 0.002 cm. Both equations are based on formulas describing a free fall of particles in the zone behind moving bubbles either in a laminar (Eq.5) or turbulent (Eq.6) water flow (Drzymala 1994).

To find out whether or not the observed hydrophobicity is distorted by the mechanical carryover the values of D_{max} for multi-particle flotation were used to calculate parameter L_H and its values are given in Table 2. According to Table 2 the L_H values for all material except bituminous shale are greater than 0.023 cm. It means that the determined hydrophobicity is not affected by the mechanical carryover. In the case of bituminous shale the value of L_H is equal to 0.021 pointing to its hydrophilicity. The hydrophilicity of bituminous shale very likely results from a high content of non-carbonaceous materials in the shale.

When the particles are hydrophobic they may aggregate and float together. It was determined that for aggregating systems the following flotometric equation holds:

$$D_{max}\left(\rho_p - \rho_w\right) = L \qquad (7)$$

and the values of L can be as high as 0.44 g/cm^2 (Lekki, Drzymala 1991). The estimation of the contact angle based on the D_{max} values for aggregating systems is a complex task. It was found, however, that for contact angles smaller than 25°, as is our case (Table 2), the aggreagation is negligible and D_{max} values for flotation of individual and a collection of particles are identical or similar (Drzymala, unpublished).

It can be interesting to add that sulfides from other Polish deposits usually have greater natural hydrophobicity. For instance, the contact angle for galena from the galena-sphalerite deposit of Olkusz is equal to about 10° because the maximum size of floating galena particles (D_{max}) is equal to 0.225 mm. It should be added that the native flotation of sulfides can be as high as for elemental sulfur which has the flotometric contact angle equal to 43°. Such a high native flotation is observed, for instance, for pyrite from Huanzala, Peru (Drzymala 1994b).

The presented in this work parameters characterize collectorless flotation and hydrophobicity of individual particles as well as particles being in contact with other particles of the same sulfide. The hydrophobicity and native flotation may significantly change when a given sulfide is in contact with another mineral, especially with another sulfide. Still greater alteration of the surface properties may occur when separation of a sulfide by flotation is attempted from complex mixtures of different minerals or natural ores. Therefore, the conclusions based on flotation results for mono-mineral systems not always can be extended to polymineral mixtures and ores.

CONCLUSIONS

It results from flotometric tests carried out with sulfide particles at pH =
= 6.5—6.9 and at natural E_h equal to 0.530—0.560 mV that djurleite, chalcopyrite,
galena, djurleite-bornite, chalcocite, and covellite from the Fore-Sudetic Copper
Region of SW Poland are only slightly hydrophobic and their contact angle is
between 2.2° and 17°.

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BEZKOLEKTOROWA FLOTOWALNOŚĆ SIARCZKÓW WYSTĘPUJĄCYCH W PRZEDSUDECKIM ZŁOŻU MINERAŁÓW MIEDZI POŁUDNIOWO-ZACHODNIEJ POLSKI

Streszczenie

Wykorzystując maksymalny rozmiar ziarn flotujących w jednopęcherzykowym
flotowniku Hallimonda zawierającym wodę o pH naturalnym równym 6,5—6,9
i potencjale redox wynoszącym 0,530—0,560 mV wyznaczono flotowalność i hy-
drofobowość badanych siarczków. Ustalono, że flotacja i hydrofobowość siarczków,
wyrażone za pomocą tzw. kąta zwilżania, rosły w kolejności: djurleit (2,2°) ~
chalkozyn (2,4°) ~ kowelin (3,7°) < chalkopiryt (6,9°) ~ galena (7,6°) ~ djurle-
it-bornit (8,4°), < bornit (12°—17°). Łupek bitumiczny, który współwystępuje
z minerałami siarczkowymi, został zaliczony do substancji hydrofilnych.