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CONTACT ANGLE OF COPPER-BEARING SHALES USING THE SESSILE DROP AND CAPTIVE BUBBLE METHODS IN THE PRESENCE OF SELECTED FROTHERS

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Abstract: This paper describes the measurement of contact angle of copper-bearing shales. The values of advancing and receding contact angles were determined using the sessile drop and captive bubble methods in the presence of aqueous solutions of acetal and pyridine and distilled water. Both methods demonstrated that the tested substances had only minor impact on the surface hydrophobicity of copper-bearing shales expressed by contact angle. The tests carried out proved that neither acetal nor pyridine may be classified to the collecting reagents because none of them improves hydrophobicity of copper-bearing shales. These reagents are only flotation frothers.

Keywords: contact angle, advancing contact angle, receding contact angle, flotation, copper-bearing shales

INTRODUCTION

The extracted mineral undergoes a series of processing operations as grinding, separation and beneficiation (Łuszczkiewicz et al., 1989; Blaschke et al., 1983). Selection of adequate processing methods depends on the mineral characteristic. The applied method on mineral, mineralogical and petrographic nature of the material to concentrate, as well as presence of other minerals and grain distribution. Numerous methods of mineral separation include grinding, screening, hydraulic and pneumatic classification, thin film separation, gravity separation, magnetic separation, electro-

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static separation, flotation, coagulation, flocculation, oil agglomeration, and biological or chemical beneficiation (Drzymała, 2007). Hydrophilicity and hydrophobicity are the result of molecular interactions occurring between molecules of water and other substances (Drzymała et al., 2008). Contact angle is the measure of hydrophobicity. Contact angle is defined as the angle between tangent to the liquid drop surface originating from the three phase solid/liquid/gas contact line and the solid surface measured across the liquid phase. The gas bubble can be used instead of the liquid drop and definition is the same. The value of contact angle may be expressed as the angle between gaseous and solid phase through a liquid phase and the angle between solid and liquid phase through a gaseous one. Hydrophillic surfaces are characterized by the work of spreading W_s , which equals (1) (Drelich et al., 2011):

$$W_s = \gamma_s - \gamma_l - \gamma_{sl} > 0 \quad (1)$$

where: γ_s – solid surface free energy,
γ_l – liquid surface free energy (the liquid surface tension),
γ_{sl} – solid/liquid interfacial free energy.

Drelich and co-workers (2011) proposed to classify smooth solid surfaces as hydrophilic ($\theta \cong 0$ º), weakly hydrophilic ($0 < \theta <$ (56-65º)), weakly hydrophobic ((56-65º) $< \theta <$ 90º) and hydrophobic ($90 \leq \theta < 120$).

The methods of measuring the contact angle at the surface of a solid are classified according to whether the surface of a tested mineral is perfect – smooth and polished or has some imperfections, i.e. is rough, imperfect. The contact angle can be described, for example, by the advancing, receding, equilibrium, Young contact angles and many others.

Quiescent contact angle (Fig. 1) is the angle measured at the phase interface, where sessile drop remains immobilized once seated. Advancing contact angle (Fig. 2) occurs, when the volume of sessile drop increases. Receding contact angle (Fig. 3) is determined when the drop volume decreases. The difference between the values of advancing and receding contact angles is called the "hysteresis of contact angle". It is caused mainly by imperfections and contamination of the surface of tested substance or by differences in surface conditions in terms of surface energy. Hydrophobicity is best defined by equilibrium contact angle, which is rather closer to the value of advancing contact angle (Tadmor, 2004; Tadmor, 2008; Tadmor et al., 2008; Marmur, 1992 and 2009). The contact angle value may also depend on the measurement method used and parameters such as drop or air bubble size (Tadmor, 2004; Tadmor, 2008; Tadmor et al., 2008; Marmur, 1992 and 2009; Drzymała, 2007).

Numerous research studies have been dedicated to measurement and analysis of contact angle and influence of selected frothers on floatation of copper-bearing shales (Drzymała, 2014; Szyszka, 2014; Szyszka et al., 2014a; Bednarek and Kowalczuk 2014; Szyszka et al., 2014b), but the group of reagents is still small.

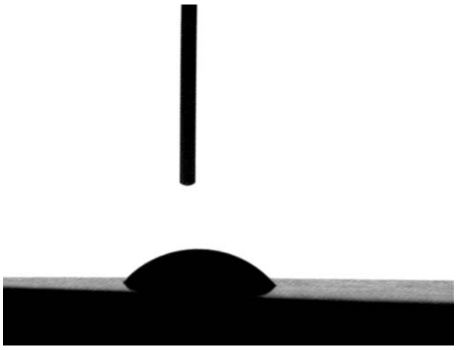

Fig. 1. Example of quiescent contact angle measurement

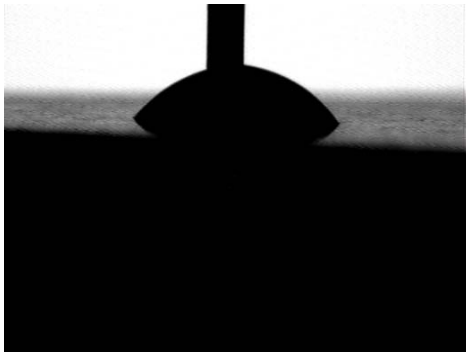

Fig. 2. Example of advancing contact angle measurement

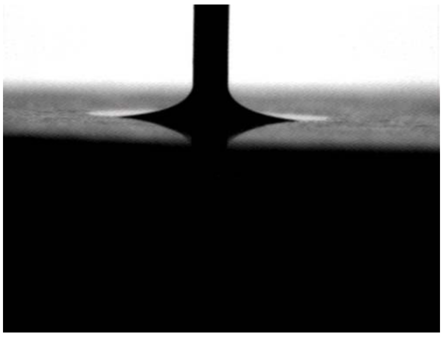

Fig. 3. Example of receding contact angle measurement

In this study, the values of contact angle of copper-bearing shales coming from Legnicko-Głogowski Copper Region (Rudna Mine) mined by KGHM Polska Miedź S.A. company were analysed. The values of advancing and receding contact angles were determined using the sessile drop and captive bubble methods in the presence of aqueous solutions of acetal (1,1-diethoxyethane, acetaldehyde diethyl acetal) and pyridine and distilled water.

EXPERIMENTAL

METHODOLOGY

Two methods of contact angle measurement: the sessile drop and captive bubble methods were used in this study. The contact angles were measured using Phoenix–300 device manufactured by Surface ElektroOptyk,(Phoenix, 2006) connected with a PC with ImageXP Software (Fig. 4).

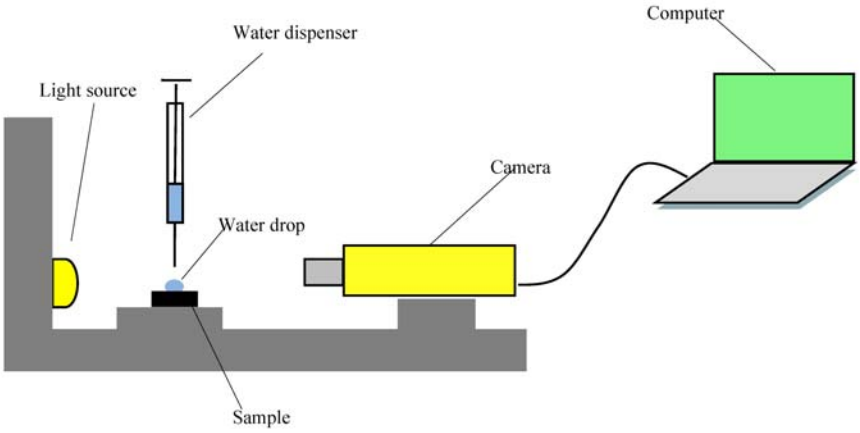

Fig. 4. Scheme system to measurement of contact angle

The measured values were read out and recorded using Phoenix-300 device and ImageXP Software. Commercially available AutoCAD Software was used to determine the contact angles. Samples of copper-bearing shales coming from Rudna Mine were used in both methods of contact angle measurement. To assure reliability of the results three samples were taken from one selected lump of a copper-bearing shale. The samples were identified with consecutive numbers 1, 2 and 3. All samples were properly ground and polished in wet conditions using abrasive paper of grit size of 100, 600, 1500, 2000 and 2500. The experiments were carried out using distilled water and two chemical reagents: acetal and pyridine. Five solutions of different concentrations were prepared for each reagent. Quiescent, advancing and receding contact angles were measured using the sessile drop method. 10–12 measurements were carried out for each sample.

Min. 15 measurements of contact angle were made for each sample using the captive bubble method.

Table 1. The structures of the investigated reagents

Properties	acetal	pyridine
Molecular formula	$C_6H_{14}O_2$	C_5H_5N
Group	Carbonyl	Amines
Purity	≥ 99%	≥ 99%
Density	0,831 g/cm^3 at 25 °C	0,982 g/cm^3 at 20 °C
Molecular weight (g/mol)	118.17	79.1
CAS number	105-57-7	110-86-1
pH	–	~10

REAGENTS USED

The contact angle of copper-bearing shales was measured in the presence of distilled water and aqueous solutions of acetal and pyridine. Chemical properties of compounds used to measure contact angle are given in Table 1. The tests were carried out in the same conditions and at constant temperature of 20 ^{o}C.

The abovementioned chemical reagents were used to measure contact angle in the following concentrations (Tab. 2).

Table 2. List of the tested reagents

Reagent	Purity %	Concentration mmol/dm^3	
Acetal	≥99	0.0703	0.3516
		0.1406	0.4923
		0.1758	
Pyridine	≥99	0.0062	0.0621
		0.0093	0.1241
		0.0124	

MEASUREMENT RESULTS AND DISCUSSION

The measurement results of contact angles demonstrates the chemical reagents used have rather minor influence on hydrophobicity of copper-bearing shales. The value of contact angle of distilled water and of all solutions of acetal and pyridine amounts to 34°, 32° and 34°, respectively. The value of contact angle of distilled water measured using the captive bubble method is 31°. The laboratory tests demonstrate that when using the sessile drop method to measure the contact angle of copper-bearing shales, the measured value of the angle decreases with increase of pyridine concentration. This relation applies to both the quiescent and advancing contact angles, but it is not so obvious for receding contact angle. For 0.5% pyridine solution the value of receding contact angle amounts to 12° and it is comparable to the value obtained for 0.05% solution of this reagent. When using acetal as a reagent, an inverse relation was observed - the values of quiescent and advancing contact angles of copper-bearing shales increased with increasing acetal concentration. The highest average value of advancing contact angle amounting to 59° was observed for 5% acetal solution. In case of receding contact angle, the use of acetal resulted in a noticeable drop of contact angle value comparing to the values obtained for pyridine and distilled water. The smallest average value of receding contact angle amounting to 9° was noted for 2% acetal solution. It is because the increase of percentage concentration of this chemical reagent does not have considerable impact on the change of surface tension of the tested material.

All average values of contact angles of tested copper-bearing shales measured using the captive bubble method are summarized in Table 3. All average values of contact angles of tested copper-bearing shales measured using the sessile drop method are summarized in Table 4.

Table 3. Contact angle values of copper-bearing shales measured using the captive bubble method

Reagent	Concentration mmol/dm^3	Average value of contact angle in solution of a given concentration, θ	Average value of contact angle, θ
Water	-	31	–
Pyridine	0.0062	29	25±3
	0.0093	26	
	0.0124	26	
	0.0622	22	
	0.1243	21	
Acetal	0.0703	29	26±2
	0.1406	28	
	0.1758	27	
	0.3516	24	
	0.4922	24	

Table 4. Contact angle values of copper-bearing shales measured using the sessile drop method

Reagent	Concentration mmol/dm^3	Average value of quiescent contact angle, θ	Average value of advancing contact angle	Average value of receding contact angle, θ
Water	-	47	56	12
Pyridine	0.0062	45	54	12
	0.0093	44	55	12
	0.0124	43	55	11
	0.0622	42	51	12
	0.1243	41	50	10
Average value of contact angle for all concentrations, θ		43±2	53±2	11±1
Acetal	0.0703	48	55	11
	0.1406	52	57	8
	0.1758	53	59	9
	0.3516	53	59	9
	0.4922	55	59	9
Average value of contact angle for all concentrations, θ		52±3	59±2	9±1

The measurement results of contact angles obtained using the captive bubble method clearly demonstrate that the higher the concentration of the reagents used, is the lower the hydrophobicity of copper-bearing shales. On the other hand, the higher the concentration of the surfactant used, the lower its influence on the contact angle values. It is also noticeable in the measurements made using the sessile drop method.

Figs. 5–6 show all the results of the measurements carried out using the sessile drop and captive bubble methods.

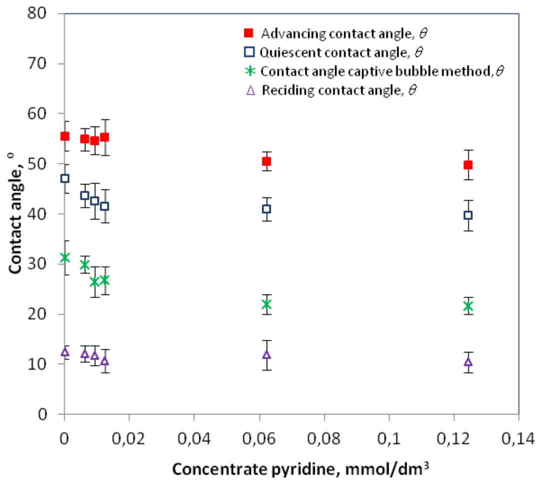

Fig. 5. Summary of the contact angle values of copper-bearing shales obtained using the sessile drop and captive bubble methods in function of pyridine solution concentration

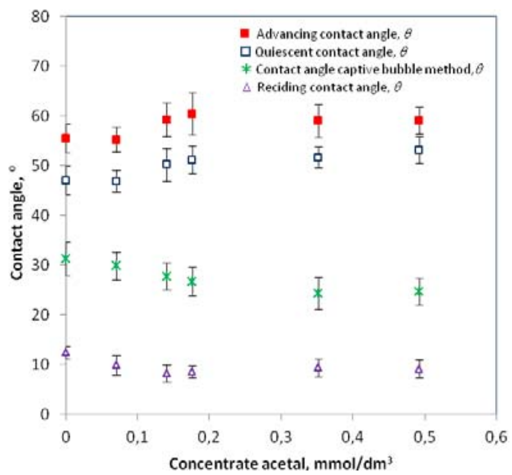

Fig. 6. Summary of the contact angle values of copper-bearing shales obtained using the sessile drop and captive bubble methods in function of acetal solution concentration

CONCLUSION

In this study the influence of selected reagent types and concentrations on measurements of contact angle of copper-bearing shales coming from Legnicko-Głogowski Copper Region (Rudna Mine) mined by KGHM Polska Miedź S.A. company was analysed.

The measurements of contact angle using both the sessile drop and captive bubble methods demonstrate that the presence of acetal and pyridine slightly modifies hydrophobicity of copper-bearing shale surface.

Both foregoing methods of measurement demonstrate that the contact angle is in inverse proportion to the increasing concentration of the tested reagents.

None of the tested reagents (neither acetal nor pyridine) may be classified as the collecting reagents, because they do not increase hydrophobicity of copper-bearing shales, and, therefore, they may perform only a frothing function in flotation process.

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