Evaluation of Contact Angle on Pyrite Surface

Lukáš KOVAL'[1], Dalibor MATÝSEK[2]

[1] Ing., Ph. D.; ENET – Energy Units for Utilization of non Traditional Energy Sources, VSB – TUO 17.listopadu 15, 708 33 Ostrava – Poruba, Czech Republic; email: lukas.koval@vsb.cz
[2] Dr. Ing.; Institute of Geological Engineering, Faculty of Mining and Geology, VSB – TUO 17.listopadu 15, 708 33 Ostrava – Poruba, Czech Republic; email: dalibor.matysek@vsb.cz

Summary

In the present paper, the contact angle measurements using six different xanthate solutions and distilled water were studied on twelve polished pyrite surfaces using sessile drop method. The 10% solutions of three potassium and three sodium xanthates were used. The pyrite samples from six countries and ten different deposits were utilized. The chemical composition of pyrites was studied using EDX microanalysis which proved that pyrite samples were not heterogenic. No relation or dependence between the contact angle and the chemical composition (i.e., Fe:S ratios) was found. The average values of contact angles measured using potassium and sodium xanthates were lower than the values of contact angle measured using distilled water. From these measurements can be concluded, that the pyrite samples are favourably wetted by either potassium or sodium xanthates than distilled water in flotation environment. The comparison of potassium and sodium xanthates showed better suitability of the potassium xanthates for the possible pyrite flotation (lower contact angle was measured on eight out of twelve samples for potasium xanthates). Pyrite samples Sokolov, Jachymov and Kutna Hora showed the lowest average contact angle values from all xanthates using potassium amyl xanthate (PAX) with average values of 34,80°, 42,94° and 31,01° respectively. The sodium xanthates would be more appropriate for the Navajun 2 and 3, Jachymov Sadon, and Norilsk pyrite samples. Very small differences in average contact angle values were obtained when potassium/sodium ethyl and isobutyl xanthates were compared. The minimum average values of contact angle for six out of twelve samples and for five out of eight samples in hydrothermal deposits were measured using ethyl xanthates what makes them the most suitable collectors for the pyrite samples from hydrothermal deposits and for pyrites in general. Even smaller variation in the results was showed using isobutyl xanthates with the highest average values of contact angle what makes them not suitable as the collectors for pyrite samples used in this study. The average value of contact angle measured using SIBX was 58,50°.

Keywords: contact angle, pyrites, potassium and sodium xanthates, sessile drop method

Introduction

Pyrite originates under different conditions and is the most widely occurring sulphide mineral [1]. It is also present in different ore deposit formations where it often represents a gangue mineral [2]. The pyrite/aqueous interaction is very important in extractive metallurgy, e.g. gold leaching from complex sulfide ores, sulfide mineral separation, coal preparation, geochemistry as well as in acid mine drainage [3]. In such procedures various agents are needed to improve the separation process of minerals. Xanthates are commonly used as pyrite collectors in the froth flotation [4] [5] [6] and [7]. The separation process is affected not only by the flotation agents but by the surface properties of pyrite as well [8].

Wettability of the mineral surface is one of the most important properties in the separation process [9]. The wettability of mineral surface is expressed by a physical parameter called contact angle, which is the measure of hydrophobicity/hydrophilicity [10]. The contact angle is explained as a balance of forces on a three phase contact line [11] and it is shown in Figure 1.

This relationship was first recognised by Young [12] and, therefore is known as the Young's equation (Eq.1).

$$\gamma_{s/v} = \gamma_{s/l} + \gamma_{l/v} \cdot \cos\theta_{Y} \qquad (1)$$

The difference between hydrophobic and hydrophilic mineral surface characteristics can be expressed by a contact angle value. The surfaces with the contact angle of 90°θ and higher are considered hydrophobic and the surfaces with the contact angle lower than 90°θ are considered hydrophilic. In general the lower contact angle, the better wetting [13]. The contact angle can be measured using different methods, nevertheless sessile drop method and captive bubble method are the most frequently used ones for the mineral surfaces [14].

Materials and methods

A list of used pyrites with the genesis of ore-deposits, the occurrence of accompanied elements and a country of origin are given in Table 1.

Mineral pyrite samples were acquired from the Geological Pavilion of Prof. F. Pošepný, VSB – TU Ostrava, Czech Republic. All samples were of high purity. Large pieces were cut into smaller sizes. The chemical analysis of pyrite samples is given in Table 2.

Xanthates samples: Potassium Amyl (PAX), Potassium Ethyl (PEX), Sodium Isobutyl (SIBX) and Sodium Isopropyl (SIPX) were provided by Cheminova, Denmark. Potassium Isobutyl (PIBX) and Sodium Ethyl (SEX) xanthates were purchased from Hoechst, Germany. All potassium and sodium xanthates used were of analytical grade. The 10% xanthates solutions and distilled water were applied during contact angle measurements.

Contact angle measurements were carried out using the Attension Theta tensiometer Biolin Scientific Oy (Finland). The sessile drop method was used in all experiments. The size of the liquid droplet was maintained constant at 5μL. The contact angles on both sides of the droplets were

Tab. 1 Genesis of ore-deposits

Tab. 1 Pochodzenie złóż rudy

Genesis of deposit	Formation	Deposit	Country of origin
Hydrothermal	Pb-Zn-Cu (+Ag)	Kutna Hora	Czech Republic
	Ni-Co-As-Bi (+U)	Jachymov	Czech Republic
	Fe-Cu±Hg±Ni,Co,Ag	Kokava,	Slovakia
	Pb-Zn (+Ag)	Sadon	Russian Federation
	Au	Guizhou	Peoples Republic of China
Sedimentary	Marl of cretaceous age	Navajun (1,2,3)	Spain
	Sediments of carboniferous age, coal	Sokolov	Czech Republic
Metasomatic	Talc	Hnusta	Slovakia
	Magnesite-talc	Obersdorf	Austria
Magmatic	Ni-Cu-Pd ± Pt	Norilsk	Russian Federation

Tab. 2 Elemental composition of pyrite samples

Tab. 2 Skład pierwiastków w próbce pirytu

Sample	Fe	S	C	O	Na	Al	Si	Ca	Zn	Mg	Pb	As
	Wt [%]											
Pyrite*	46,60	53,40										
Kutna hora	40,10	45,89	2,56	8,95	0,28	0,20	0,30	0,37	1,35			
Jachymov	41,13	41,21	2,58	7,79		0,51	3,28	1,39	0,72	1,37		
Kokava	44,20	52,24		1,82	0,35				1,40			
Sadon	42,62	45,99	6,26	3,81		0,27	0,29	0,76				
Guizhou	44,81	53,84	1,35									
Navajun 1	44,93	53,84	1,23									
Navajun 2	45,03	54,97										
Navajun 3	46,10	53,90										
Sokolov	46,59	53,41										
Hnusta	42,03	36,22	10,67	3,52	0,21		1,07			0,74	5,55	
Oberdorf	43,34	52,74	2,73		0,42		0,16					0,61
Norilsk	44,88	45,75	9,37									

Tab. 3 Average values of contact angle

Tab. 3 Średnie wartości kąta zwilżania

Sample	SIBX	SEX	SIPX	PIBX	PAX	PEX	H_2O
	Average contact angle [°]						
Navajun 1	54,51	49,01	57,17	50,95	56,07	37,60	71,27
Navajun 2	56,88	37,93	54,68	52,63	53,19	43,01	68,77
Navajun 3	54,33	34,27	50,32	51,10	46,27	39,36	69,88
Sokolov	61,18	53,98	65,33	55,70	34,80	42,58	85,80
Hnusta	65,57	67,07	62,53	66,71	67,91	49,59	81,93
Oberdorf	62,35	71,85	67,84	57,61	58,04	59,12	84,77
Kokava	54,16	51,58	58,74	52,36	54,45	43,03	82,22
Jachymov	51,87	45,35	48,27	56,72	42,94	49,78	81,47
Sadon	61,70	54,87	41,75	66,56	54,18	68,44	74,92
Norilsk	64,30	66,49	57,94	70,15	74,77	72,21	86,94
Kutna Hora	55,93	62,97	51,02	56,48	31,01	39,09	85,47
Guizhou	59,27	62,17	54,87	57,34	59,93	46,04	80,21
AVERAGE	58,50	54,97	55,87	57,86	52,80	49,15	79,47
STD	4,49	11,83	7,42	6,50	12,59	11,53	6,55

calculated and the average value of six measurements was used. All measurements were carried out at a temperature of 25±2°C.

Samples from Sokolov, Kutna Hora, Kokava, Oberdorf and Guizhou were at first casted into mounting epoxy resin. The rest of the samples were used as received (bulk minerals) from the Geological Pavilion. Samples were polished on a rotating abrasive paper with the grit size of 600, 800, 1200 and 2500 (number of grains per inch) under running water using LaboPol-21 grinder Struers (USA). The final polishing was done on a fine textile polishing cloth using aluminium paste and Phoenix 3000, Buehler (USA). Then the samples were washed thoroughly with distilled water.

A microanalysis of all pyrite samples was performed using SEM/EDX (scanning electrone microscopy and energy-dispersive X-ray microanalysis) on Fei Quanta 650 FEG (FEI, USA).

Results and discussion

Microanalysis

The microanalysis of pyrite samples was conducted prior to contact angle measurements in order to find some differences in the chemical composition. It is well known, that the contact angle is affected by heterogeneity of minerals [15]. To avoid that, a surface area on a pure mineral pyrite grain with an approximate size of 5x5 mm was selected for the contact angle measurements on each sample. Nevertheless pyrite samples were obtained from different deposits, with a different genesis and they were associated with different minerals. Figure 2 shows the images of selected pyrite grains. Figure 2a shows an impregnation of galena and talc on pyrite, Figure 2b displays the phosphate and rare earth grains on grooved surface of pyrite crystals, whereas Figure 2c shows a lightly grooved surface of pyrite crystal with an inclusion of calcite. The grey areas in Figure

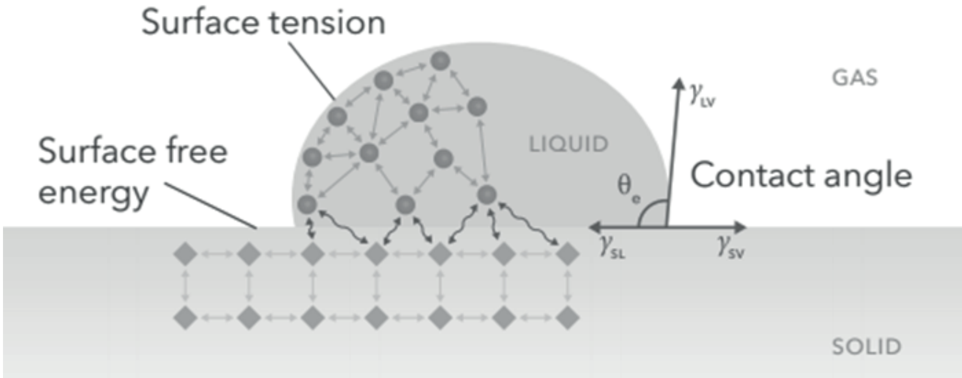

Fig. 1 Key concept of contact angle [8]
Rys. 1 Koncepcja kąta zwilżania [8]

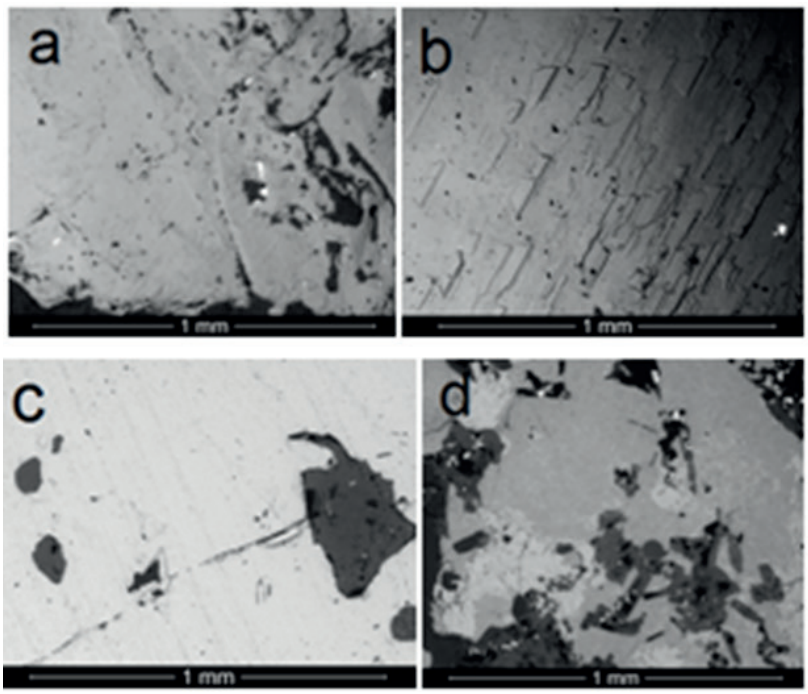

Fig. 2 Microanalysis of selected pyrite grains: Hnusta (a), Guizhou (b), Navajun (c), Jachymov (d)
Rys. 2 Mikroanaliza wybranych ziaren pirytu: Hnusta (a), Guizhou (b), Navajun (c), Jachymov (d)

2d represent pyrite, the slightly lighter grey areas represent pyrhotine, the dark grains represent calcium siderite, and finally the small white grains represent sphalerite.

Contact angle measurements

The standard deviation and average values of contact angle for all xanthates solutions and water for each pyrite sample are shown in Table 3.

As it can be seen, a wide range of contact angle values was obtained using different agents. Sulphides may show a different value of contact angle within the individual grains which is probably caused by heterogeneity of particles [16]. The pyrite samples that were used in this study were not heterogenic (on selected spots where contact angle was measured) as it was confirmed by the microanalysis tests using EDX method.

However, the contact angle values that were measured using distilled water for different pyrite samples varied from 68,77° to 86,94°. No relation or dependence between the contact angle and the genesis of the deposit, or different chemical composition (i.e., Fe:S ratios) were found. The differences must be caused by the other factors. To compare all measured values of contact angle, the standard methodology based on the anomaly threshold determination ($\bar{x}$±2STD) was used. All presented results met this criterion.

Results divided into two different groups (potassium and sodium xanthates) are shown in Figures 3 and 4. It seems that potassium and sodium xanthates react with different pyrite samples almost in the same way.

The dfferences in the average values of contact angle using potassium xanthates were observed for the Sokolov, Jachymov and Kutna Hora samples. These samples showed the lowest average values of contact angle of 34,80° and 42,94° using PAX, and the lowest measured value of 31,01° from all xanthates, respectively. Very small differences in the average values of contact angle were measuered for the Oberdorf sample using potassium xanthates; the val-

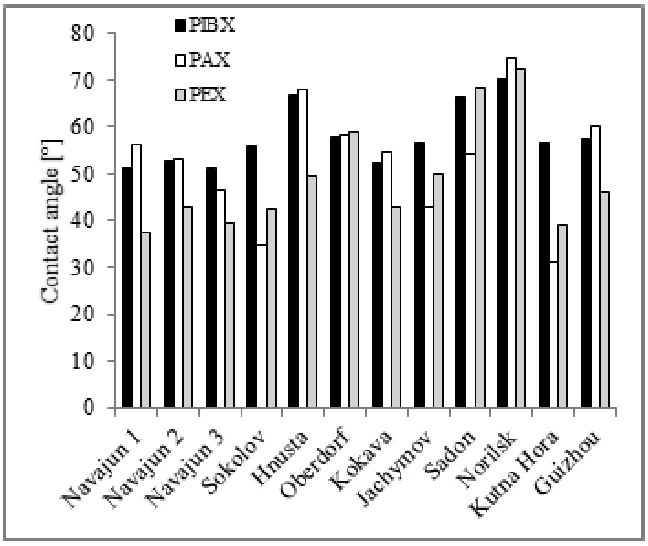

Fig. 3: Average value of contact angle - potassium xanthates
Rys. 3 Średnia wartość kąta zwilżania – ksantogenian potasu

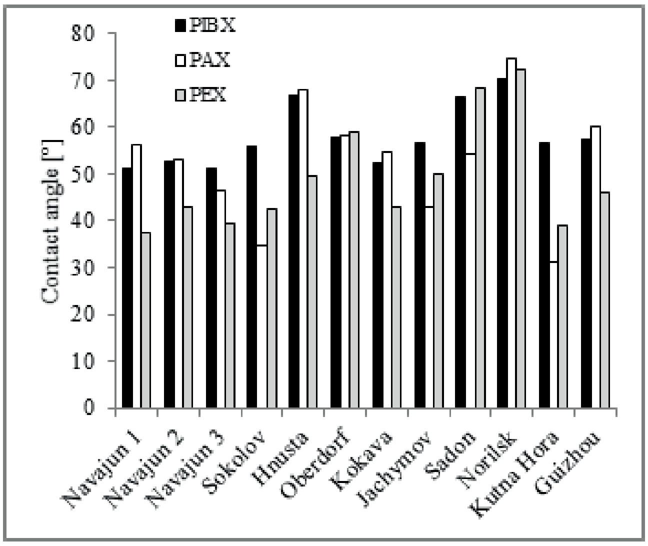

Fig. 4 Average value of contact angle - sodium xanthates
Rys. 4 Średnia wartość dla kąta zwilżania – ksantogenian sodu

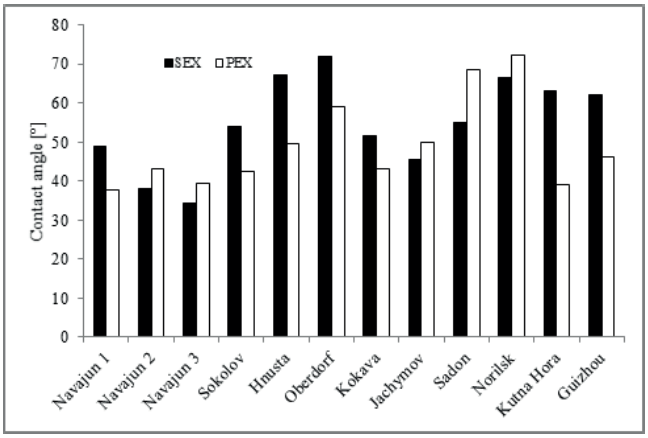

Fig. 5 Average value of contact angle - ethyl xanthates
Rys. 5 Średnia wartość kąta zwilżania – ksantogenian etylowy

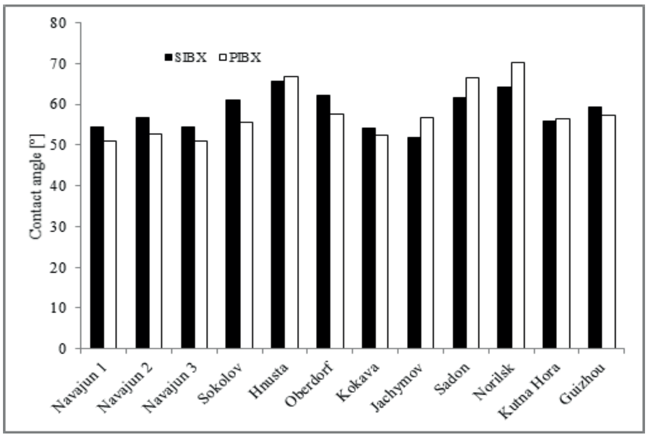

Fig. 6 Average value of contact angle - isobutyl xanthates
Rys. 6 Średnia wartość kąta zwilżania
– ksantogenian izobutylowy

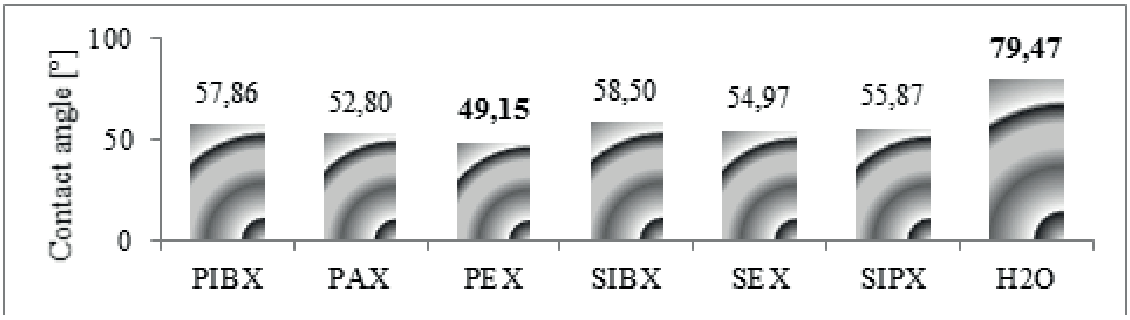

Fig. 7 Average values of contact angle using xanthates and water
Rys. 7 Średnia wartość kąta zwilżania z użyciem ksantogenianów i wody

ues were in the range of 1,6°. However, they are still in very good agreement with the lowest standard error range of 0,7 – 1,6° reported in literature [17]. Other authors have published the results with even higher standard errors in the range from ±2° up to ±5° [9] [11] and [18]. The best result of the average values of contact angle of 57,61° was obtained using PIBX for the Oberdorf sample. This result is the only one which proved that isobutyl xanthate (either sodium or potassium) is suitable collector for the pyrite sample. In general, the highest average values of contact angles using xanthates were measured for the Norilsk sample in general. The contact angle that was measured using SIPX was 57,94° which is the highest average value of contact angle still suitable for possible flotation. Best result that was obtained using SIPX was also observed for the Sadon sample, the contact angle value of 41,75° was obtained.

The differences in contact angle values were even smaller when potassium/sodium ethyl and especially isobutyl xanthates were compered. The results are shown in Figures 5 and 6.

Potassium ethyl xanthate had lower average values of contact angle than sodium ethyl xanthate. Big differences in the average value of contact angle were measured using PEX and SEX for the Hnusta, Oberdorf, Kutna Hora and Guizhou samples. The value of average contact angle varied by 17,48° for these samples. The minimum average values of contact angle were measured using PEX for the Hnusta (49,59°) and Guizhou (46,04°) samples. The differences in average values of contact angle were much smaller for the remaining measurements.

The minimum average values of contact angle of 37,93° and 34,27° was measured using SEX for the Navajun 2 and 3 samples, respectively. Ethyl xanthates seem to be the most suitable collectors for the pyrite samples from hydrothermal deposits as well as for pyrites in general. The minimum average values of contact angle for six out of twelve samples and for five out of eight samples in hydrothermal deposits were measured using ethyl xanthates. A very small variation in the results was observed using isobutyl xanthates for contact angle measurements. Both potassium and sodium xanthates showed the highest average values of contact angle and based on these results it can be concluded that they are not suitable collectors for the pyrite samples that were used in this study.

As previously mentioned, the lower the contact angle value, the greater the wettability of the mineral surface [19]. The comparison of average values of contact angle indicates that the contact angles measured using potassium and sodium xanthates are lower in all cases than the average values of contact angle measured using water (Figure 7).

The results confirmed that the pyrite samples are favourably wetted by either pottasium or sodium xanthates in water (flotation) environment. The comparison of potassium and sodium xanthates showed that, in general, potassium xanthates exhibited better results and they are more suitable for possible pyrite flotation. A lower contact angle was measured using potassium xanthates in eight measurements out of 12. The use of sodium xanthates would be more appropriate for the Navajun 2 and 3, Jachymov Sadon, and Norilsk pyrite samples. Based on the results of contact angle measurements SIBX is not suitable collector; even the average value of contact angle measured using xanthate was 58,50°.

Therefore, the results obtained in this study can be used to predict the most suitable xanthate for various pyrite samples in the flotation process. On the other hand the results do not explain the mechanism of adsorption of xanthates on pyrite surfaces. That has been the subject of other studies [20] [21].

Conclusion

The contact angle of the pyrite samples obtained from various deposits and with a different genesis using xanthates and water were studied. The sessile drop method was used. No dependence of contact angle on chemical composition was found. Based on the contact angle measurements, pyrite samples were preferentially wetted by the xanthates (either pottasium or sodium) in water (flotation) environment. In general, the potassium xanthates were more suitable. When ethyl and isobutyl xanthates were compared, ethyl xanthates seemed to be the most suitable collectors for pyrites, especially for pyrites from hydrothermal deposits. The highest average values of contact angle with a very small variation were obtained using isobutyl xanthates, which were not suitable for possible pyrite flotation except for the Oberdorf pyrite sample. However, the theory still cannot explain a number of phenomena observed in the pyrite/xanthate flotation system. Only moderate numbers of studies have been devoted to the evaluation of the pyrite-xanthate flotation system and even less to the utilization of xanthates for the measurement of the contact angle of pyrite surface.

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Literatura - References

1. Klein, C. et al.: *The 23rd edition of the manual of mineral science: (after James D. Dana). 23rd ed. Hoboken, N.J.: J. Wiley, c2008, xxi, 675 p. ISBN 04-717-2157-3*
2. He, M.-F., et al.: *Pyrite depression in marmatite flotation by sodium glycerine-xanthate. Transactions of Nonferrous Metals Society of China. 2011, vol. 21, issue 5, s. 1161-1165*
3. Raichur, A.M. et al.: *Quantifying pyrite surface oxidation kinetics by contact angle measurements. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2000, vol. 167, issue 3, s. 245-251*
4. Wang, X.-H., Forssberg K.S. Eric. *Mechanisms of pyrite flotation with xanthates. International Journal of Mineral Processing. 1991, vol. 33, 1-4*
5. Miller J.D. et al.: *The low-potential hydrophobic state of pyrite in amyl xanthate flotation with nitrogen. International Journal of Mineral Processing. 2002, vol. 67, 1-4, s. 1-15*
6. Sui, C. C. et al.: *Xanthate adsorption on Pb contaminated pyrite. International Journal of Mineral Processing. 1997, vol. 49, 3-4, s. 207-221*
7. Chandra A. P. et al.: *Copper and xanthate adsorption onto pyrite surfaces: Implications for mineral separation through flotation. International Journal of Mineral Processing. 2012, 114-117, s. 16-26*
8. Chau, T.T. *A review of techniques for measurement of contact angles and their applicability on mineral surfaces. Minerals Engineering. 2009, roč. 22, č. 3, s. 213-219. ISSN 08926875*
9. Ding, L.-P. *Investigation of Bituminous Coal Hydrophobicity and its Influence on Flotation. Energy. 2009-11-19, vol. 23, issue 11, s. 5536-5543*
10. Chau, T.T. et al.: *A review of factors that affect contact angle and implications for flotation practice. Advances in Colloid and Interface Science. 2009, roč. 150, č. 2, s. 106-115. ISSN 00018686*
11. Ofori, P. et al.: *Assessing the Hydrophobicity of Petrographically Heterogeneous Coal Surfaces. Energy. 2010-11-18, vol. 24, issue 11, s. 5965-5971*
12. Young, T. *An Essay on the Cohesion of Fluids. Philosophical Transactions of the Royal Society of London. 1805-01-01, vol. 95, issue 0*
13. Dey, S. *Enhancement in hydrophobicity of low rank coal by surfactants — A critical overview. Fuel Processing Technology. 2012, vol. 94, issue 1, s. 151-158*
14. Baek, Youngbin, et al.: *Measuring hydrophilicity of RO membranes by contact angles via sessile drop and captive bubble method. Desalination. 2012, vol. 303, s. 23-28*
15. Lin, F.Y.H. a Li D. *The effect of surface heterogeneity on the drop size dependence of contact angles. Chemical Engineering Science. 1995, vol. 50, issue 16, s. 2633-2639*

16. Muganda, S., M. Zanin a S.R. Grano. Benchmarking flotation performance: Single minerals. International Journal of Mineral Processing. 2011, vol. 98, 3-4, s. 182-194
17. Shojai Kaveh N., E. et al.: Wettability determination by contact angle measurements: hvbB coal–water system with injection of synthetic flue gas and CO2. Journal of Colloid and Interface Science. 2011, vol. 364, issue 1, s. 237-247
18. Chipfunhu, D. et al.: The dependency of the critical contact angle for flotation on particle size – Modelling the limits of fine particle flotation. Minerals Engineering. 2011, vol. 24, issue 1, s. 50-57
19. Muganda, S. et al.: Influence of particle size and contact angle on the flotation of chalcopyrite in a laboratory batch flotation cell. International Journal of Mineral Processing. 2011, vol. 98, 3-4, s. 150-162
20. Montalti, M., Fornasiero D., RALSTON. Ultraviolet-visible spectroscopic study of the kinetics of adsorption of ethyl xanthate on pyrite. Journal of Colloid and Interface Science. 1991, vol. 143, issue 2, s. 440-450
21. Leppinen, J.O. FTIR and flotation investigation of the adsorption of ethyl xanthate on activated and non-activated sulfide minerals. International Journal of Mineral Processing. 1990, vol. 30, 3-4, s. 245-263

Wyznaczanie kąta zwilżania na powierzchni pirytu

W pracy tej badano pomiary kąta zwilżania z użyciem trzech różnych roztworów ksantatui wody destylowanej na dwunastu polerowanych powierzchniach pirytu za pomocą metody osadzania kropli. Użyty został 10% roztwór trzech ksantatów potasu i trzech ksantatów sodu. Wykorzystane zostały próbki pirytu z sześciu państw i dziesięciu różnych depozytów. Skład chemiczny pirytów był zbadany za pomocą mikroanalizy EDX, która udowodniła, że próbki pirytu nie były heterogeniczne. Nie znaleziono żadnej relacji lub zależności między kątem zwilżania i składem chemicznym (np. stosunku Fe:S). Średnie wartości kąta zwilżania zmierzone z użyciem ksantatów potasu i sodu były niższe niż wartości kąta zwilżania zmierzone z użyciem wody destylowanej. Z pomiarów tych można wnioskować, że próbki pirytu są łatwiej zwilżane za pomocą ksantatów potasu lub sodu niż za pomocą wody destylowanej w środowisku flotacyjnym. Porównanie ksantatów potasu i sodu wykazało lepszą przydatność ksantatu potasu w możliwej flotacji pirytu (niższy kąt zwilżania został zmierzony w ośmiu z dwunastu próbek dla ksantatu potasu). Próbki pirytu Sokolov, Jachymov i Kutna Hora wykazały najniższe średnie wartości kąta zwilżania ze wszystkich ksantatów z użyciem potasowego amylu ksantatu (PAX) ze średnimi wartościami odpowiednio 34,80°, 42,94° i 1,01°. Ksantaty sodu mogą być bardziej odpowiednie dla próbek pirytu Navajun 2 i 3, JachymovSadon i Norilsk. Bardzo małe różnice w wartościach średnich kąta zwilżania zostały uzyskane gry potasowy lub sodowy etyl i izobutyl ksantatu były porównywane. Minimalne średnie wartości kąta zwilżania dla sześciu z dwunastu próbek i na pięciu z ośmiu próbek z depozytów hydrotermalnych były zmierzone z użyciem etylu ksantatu co czyni je najbardziej odpowiednimi kolektorami dla próbek pirytu z depozytów hydrotermalnych i pirytów w ogóle. Jeszcze mniejsze wahania wyników wykazano używając izobutylu ksantatów lecz uzyskano najwyższe średnie wartości kąta zwilżania co czyni je niewłaściwymi kolektorami dla próbek pirytu użytych w tym badaniu. Średnia wartość kąta zwilżania zmierzonego z użyciem SIBX wynosiła 58,50°.

Słowa kluczowe: kąt zwilżania, piryty, ksantogeniany potasu i sodu, metoda osadzonej kropli