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THE USE OF DIELECTRIC BARRIER DISCHARGE TO REGULATE THE TECHNOLOGICAL PROPERTIES OF CHALCOPYRITE AND SPHALERITE

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ABSTRACT – The modification of structural and chemical properties of natural chalcopyrite and sphalerite as a function of dielectric barrier discharge (DBD - treatment) parameters were investigated experimentally with the help of the adsorption of acid and base indicators, sorption and flotation tests. It was determined that DBD - treatment during of 5 - 30 second results to the increasing of the electron - accepting properties of chalcopyrite and sphalerite. Thus, single mineral flotation tests showed that DBD - treatment resulted to the improvement of the sorption activity of the sphalerite and chalcopyrite and floatability.

Keywords: Chacopyrite, Sphalerite, Dielectric Barrier Discharge, Floatability, Surface Properties.

INTRODUCTION

The problem of selective separation of bulk concentrates of sulfides minerals is very important. Ionizing radiations and high - energy impacts (accelerated electrons, neutrons, gamma rays, low - temperature plasma, high - voltage nanosecond pulses, etc.) are viewed as additional operations in mineral processing for directed changes in the mechanical, electrophysical, physicochemical and technological properties of non-ferrous, noble and rare metal minerals, calcium bearing minerals *etc.* [1]. The use of high - power nanosecond electromagnetic pulses (HPEMP - treatment) and low - temperature dielectric barrier discharge plasma (DBD - treatment) for treatment of minerals increases the efficiency of opening mineral intergrowths and causes the development of solid - phase chemical reactions on the surface of sulfide minerals with the formation of micro - and nanophases in the form of hydrophobic elemental sulfur and various hydrophilic oxygen - containing compounds, which helps to increase the selectivity of flotation separation of sulfides with similar physicochemical properties [1].

EXPERIMENTAL

In this study, two natural mineral samples of high purity were used: chalcopyrite ($CuFeS_2$) and sphalerite (ZnS) which came from the Dalnegorskoe ore field (Primorye,

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Russia). The mineral samples contain small amount of other components. The XRF analysis was used to determine the chemical composition of samples (Table 1).

The DBD - treatment of mineral samples was carried out in air and the following parameters of the pulses initiating the discharge: leading edge pulse time — 250 - 300 ns, pulse duration — 8 µs, voltage on the electrodes in the barrier discharge cell— 20 kV, pulse repetition frequency — 16 kHz (10 kHz;5 kHz,8 kHz;2 kHz) the range of variation of the DBD sample treatment time 10 - 100 s; the length of the interelectrode gap was about 5 mm. The mineral samples were placed in the discharge and the working surfaces of the samples were located on the surface of the dielectric barrier.

The Hammett indicator adsorption method was used to differentiate and study the acid - base properties of the mineral surface [1]. The list of indicators, pKa values, working concentrations of indicator' solutions, and wavelengths corresponding to the absorption maximum are presented in Table 2.

Table 1 Chemical composition of the mineral samples

Element present (mass %)									
	Cu	**Fe**	**Zn**	**S**	**Pb**	**Ca**	**Mn**	**Mg**	**As**
$CuFeS_2$	28.54	27.54	1.91	29.17	3.19	0.70	0.04	0.01	0.006
ZnS	0.29	4.08	<50.00	29.30	6.61	0.19	0.129	0.02	0.153

Table 2 Indicators names and parameters

Indicator	**pKa**	**λ max, nm**	**C_{ind}, mmol /l**
dinitroaniline	-4.4	340	1.20
brilliant green	1.3	610	0.33
bromophenol blue	4.1	590	0.08
bromocresol purple	6.4	590	0.16
bromothymol blue	7.3	430	0.36
Indigo carmine	12.8	610	0.40

The optical density of the initial indicator solution D_0 and the indicator solution after adsorption - desorption equilibrium with the mineral sample D_1 were measured spectrophotometrically (Shimadzu UV - 1700). The change in the optical density of the indicator solution as a result of the interaction of the studied mineral with distilled water D_2 was also taken into account, which made it possible to exclude this factor during the analysis of the results. The concentration of surface active centers, equivalent to the amount of adsorbed amount of indicator q_{pKa}, and it was determined using the following formula [3]:

$$q_{pK\alpha} = \frac{C_{ind} V_{ind}}{D_0} \left[\frac{|D_0 - D_1|}{m} \pm \frac{|D_0 - D_2|}{m} \right] \quad (1)$$

where C_{ind} is the indicator concentration (mol/l), V_{ind} is the indicator volume (ml), m is the sample weight (g). The signs "+" and "-" correspond to the opposite and unidirectional changes of D_1 and D_2, respectively. According to [3], indicators with the lowest (negative) pKa values are selectively adsorbed on the active centres of the Lewis basic type, containing an unshared electron pair and capable of capturing a proton during hydrolytic dissociation of a water molecule. As the pKa of indicators increases, their selective adsorption occurs on Bronsted acidic centers (pKa = 0 - 7, surface OH groups with a tendency to split off a proton), Bronsted basic (pKa = 7 - 14, surface OH groups with a tendency to split off the entire hydroxide) and Lewis acidic centers (pKa ≥ 14, atoms with a free orbital, capable of capturing a hydroxyl with dissociative adsorption of water).

Sorption activity of chalcopyrite and sphalerite samples were studies with DRIFT spectroscopy IR Affinity (Shimadzu) equipped with diffuse reflection attachment DiffusIR (Pike Technologies).

Single mineral flotation test was carried out using 1.0 g mineral sample in a special 20-ml laboratory flotation cell. Butyl potassium xanthate (30 g/t) was used as a collector and MIBC as frother. All flotation tests were performed at pH 9.5 after adjustment using CaO solution. The accuracy of recovery results can be estimated around 2 %.

RESULTS AND DISCUSSION

The influence of DBD - treatment parameters on flotation properties chalcopyrite and sphalerite was studied carefully (Table 3). The obtained results showed that floatability increase for both minerals considerably as a function of the treatment duration for the size fraction of - 44 µm. While for the size fraction of -100 + 50 µm there is no significant changes in the flotation properties of minerals with variations of DBD - treatment parameters. It occurs due to rising of the specific surface area of the crushed sample with decreasing particle size; also, the specific surface area of the particles increases due to the increase in the number of microdefects (pores, microcracks, electrical breakdown channels) formed as a result of the action of the DBD - treatment. Therefore, the efficiency of DBD - treatment of minerals increases with decreasing mineral size and increasing number of particles involved in the process of exposure to such DBD - treatment factors as a strong electric field, ion wind, increased particle mobility in the interelectrode gap [1, 2], as well as the increasing action of chemically active plasma particles (O_3, singlet oxygen $O_2(a^1\Delta_g)$, H_2O_2 and OH) [3, 5], formed in interparticle microdischarges [4].

Table 3 Influence of DBD - treatment parameters of the chalcopyrite and sphalerite floatability (size fraction -44 µm)

	2.0 kHz	5.8 kHz	10.0 kHz	16.0 kHz
8µs	$CuFeS_2$ ↑ 8-14 % ZnS=const	$CuFeS_2$ ↑ 7-16 % ZnS↑ 6-10 %	$CuFeS_2$ ↑ 7-14 % ZnS↑ 2-15 %	$CuFeS_2$ ↑ 4-16 % ZnS↑ 10-17 %
4µs	$CuFeS_2$ ↑ 6-18 % ZnS= const	$CuFeS_2$ ↑ 4-18 % ZnS = const	$CuFeS_2$ ↑ 9-13 % ZnS↑ 4-11 %	$CuFeS_2$ ↑ 5-17 % ZnS↑ 5-10 %

As it, follows from the Table 3 there are DBD - treatment conditions those results to the rising of the floatability for the both minerals in 10 - 20 %. At the same time, obviously, there are the treatment conditions that leads to the growth of the chalcopyrite floatability only. It means that the DBD - treatment can be used in the process of the bulk or copper concentrate separation process depending on goals.

For the DBR - treatment mode that results to the highest simultaneous recovery of chalcopyrite and sphalerite into the froth flotation product, the effect of DBR - treatment on the acid-base properties of the surface were studied. The obtained results are presented in the Figure 1.

As can it be seen from the obtained results for sphalerite, as a consequence of DBD - treatment, the negative charge of the mineral surface drops because the number of active centers with pKa = 0.29 (electron duplet) reduce. More over the number of active centers p_{Ka} = 12.0 increases. The appearance of the active centers with p_{Ka} = 12.0 indicates an increase in the acceptor force of the mineral surface. A similar changes was identified for chalcopyrite surface (Figure 1). In other words, as a result of the DBR - treatment of chalcopyrite and sphalerite, firstly, the negative charge of the surface of the minerals decreases, and secondly, the acceptor capacity of the surface increases.

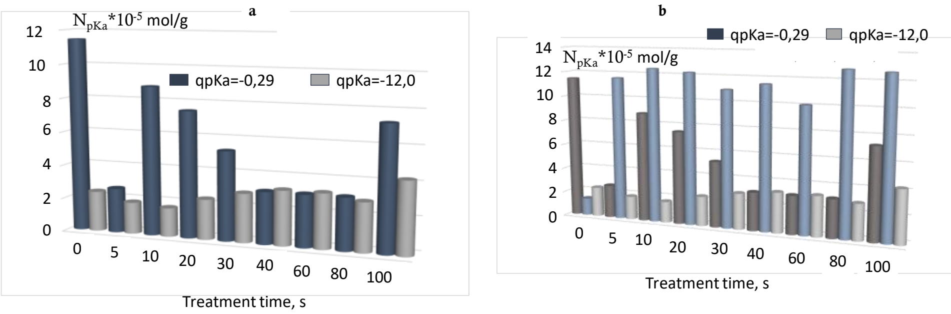

Figure 1 Influence of DBD - treatment parameters on the concentration of the surface active centers.

The alterations in the in the energy state of the mineral surface caused by DBR - treatment should have contributed to a change in its sorption activity in relation to reagents with electron-donor properties. Therefore, the influence of DBR - treatment on the sorption activity of chalcopyrite and sphalerite towards butyl xanthate was studied using DRIFT. Figure 2 shows the obtained results. The vibrations of 1043 cm^{-1}1201cm^{-1} 1267 cm^{-1} in Figure 2a belong to vibrations of the adsorbed collector hydrocarbon skeleton. The peak positions indicates that collector molecules is adsorbed in the form of dixanthogen. A similar picture is observed for sphalerite surface (Figure 2b).

The calculation of the of the integrated band intensities attributed to the vibrations of potassium butyl xanthate bands demonstrates that the after the DBD - treatment the integrated intestines of bands raised in 1.2 - 1.3 times as compared to untreated sample that means that the sorption of collector on the mineral surface increased.

The applicability DBD - treatment for intensification of the copper recovery from natural mineral objects was confirmed by using flotation of copper middlings. Table 4 presents the data obtained.

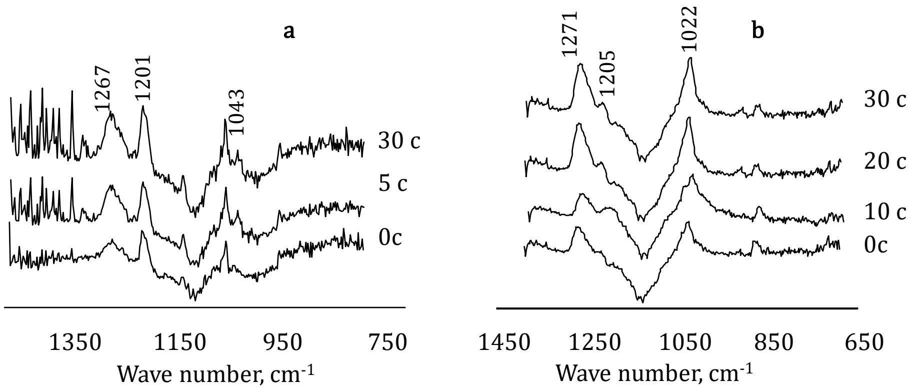

Figure 2 Influence of DBD - treatment parameters on the sorption activity of chalcopyrite and sphalerite.

Table 4 Influence of DBD - treatment on recovery of copper from middlings obtained from copper - zinc ore of the Alexandrinsky deposit

Treatment time	product	weight		Cu	εCu$_{concentrate.}$, %	εCu$_{tails.}$, %
0		g.	γ,%	β, %		
	concentrate	20,56	41,33	14,76	**48,80**	
	tails	29,19	59,21	11,08		51,20
10 s	total	49,75	100			100
	concentrate	30,46	60,97	14,20	**69,73**	
	tails	19,50	39,03	9,94		30,27
30 s	total	49,96	100			100
	concentrate	25,45	50,86	14,74	**58,89**	
	tails	24,59	49,14	10,71		41,11
	total	50,04	100			100

The table shows that preliminary DBD - treatment in a low-temperature plasma field allows to increase the recovery of copper in the froth product of the flotation. The recovery of copper in the froth product was about 48 % before the treatment. The DBD - treatment during the 10 s allows to improve the recovery of the copper to 69 %, i.e. by 20 %. The DBD - treatment during 30 s results the rising of the copper recovery to 58, 8%, i.e. by 10 % as compared to untreated sample.

CONCLUSION

It was defined that dielectric barrier discharge (DBD - treatment) can change the floatability of monomineral chalcopyrite and sphalerite (-44 µm). DBR - treatment can be used to improve the selectivity of chalcopyrite and sphalerite separation. It was identified that there are the DBD - treatment conditions where the flotation of chalcopyrite increases in 5 - 18 % while the floatability of sphalerite is invariable (duration of initiating discharge pulses $\tau_{imp.}$ = 4 and 8 µs, pulse repetition frequency $f_{imp.}$= 2 kHz). At the same time the another DBD - treatment parameters can be used for the recovery increasing for both minerals in 5 - 17% ($\tau_{imp.}$= 8 µs, $f_{imp.}$=16 kHz).

With application of Hamet' indicators adsorption method, it was defined that the changes in the flotation properties of chalcopyrite and sphalerite as a result of DBD - treatment results from the acid - base (donor-acceptor) properties of the minerals surface. Because of DBD - treatment, the negative charge of the minerals surface decreases, and the acceptor force of the surface increases. It results to the improvement of the sorption ability of the mineral surface towards butyl xanthate and as the consequence to the improvement of the floatability.

The results of the flotation of the middlings obtained from copper - zinc ore of the Alexandrinsky deposit showed that DBD - treatment allow to increase the recovery of copper in the concentrate by 10.1 - 20.9 %.

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