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THE EFFECT OF SULPHITE ON THE XANTHATE-INDUCED FLOTATION OF COPPER-ACTIVATED PYRITE

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The effect of sulphite ions on the xanthate-induced flotation of copper-activated pyrite has been studied. Various techniques have been used to identify the plausible mechanisms of interaction of sulphite with both collector and pyrite surface. It was found that sulphite depressed the xanthate-induced flotation of copper-activated pyrite with nitrogen or air purging at pH 7. However, the depression effect was greater when air was used. Solution and spectroscopic studies indicated that sodium bisulphite interacted with the pyrite surface, as well as with isobutyl xanthate in solution and its adsorbed state. Based on the results obtained, a combination of possible mechanisms has been proposed to explain the depressing effect of sulphite on copper-activated pyrite. It was suggested that both the decomposition of the xanthate in solution via perxanthate formation and dixanthogen desorption from the pyrite surface were responsible for the pyrite depression. Furthermore, iron hydroxy species were formed on the pyrite surface, rendering it hydrophilic, thus preventing the formation of bubble-pyrite particle aggregates.

Key words: pyrite, flotation, sulphite, depressants

INTRODUCTION

Froth flotation is widely used for separating sulphide minerals in complex ores. Typical examples in sequential separation of sulphides include sphalerite and pyrite depression during galena and/or chalcopyrite flotation. A common problem for copper-zinc-iron mineral selectivity is related to the unintentional activation of pyrite and sphalerite by copper ions. Cyanide addition is usually employed in industrial practice for complexing and removing copper ions from unwanted sulphides in the selective flotation of minerals. However, the use of cyanide causes environmental and

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safety problems. Sulphur-oxy species, such as sulphite (SO_3^{2-}), bisulphite (HSO_3^-), metabisulphite ($S_2O_5^{2-}$) or sulphur dioxide (SO_2), have been used in some mineral processing operations as depressants instead of cyanide.

Different mechanisms have been proposed to explain the effect of sulphite on the selective depression of sulphide minerals. In general, these mechanisms can be divided into two main categories. The first category involves interaction of sulphite ions with the mineral surface. Misra et. al (1985) suggested two mechanisms of depression including the formation of a metal sulphite hydrophilic surface layer and consumption of copper ions in solution by sulphite. As a result of this interaction, some insoluble copper sulphite precipitates are formed rendering the mineral surface hydrophilic (Misra et. al 1985). Also, it has been shown that adsorbed sulphite species interact with mineral sulphur species and this may decrease the surface hydrophobicity (Li et. al 1995). The second category includes the interaction of sulphite with collector either in solution or its adsorbed state. Yamamoto (1980) found that sulphite ions decomposed the xanthate collector in solution via perxanthate formation. Miller (1970) reported desorption of pre-adsorbed collector species such as dixanthogen by sulphite ions. Illyuvieva et. al (1984) proposed a mechanism involving the consumption of dissolved oxygen by sulphite. In this particular case, the Eh of the solution might be reduced because of sulphite oxidation to sulphate. Due to the lack of oxygen in solution, the formation of dixanthogen and collector adsorption may also be minimised (Illyuvieva et. al 1984).

Still, the action and mechanisms of sulphur-oxy reagents are not well understood, particularly when applied to copper-activated pyrite. The aim of this current work is to study the effect of sulphite on the xanthate-induced flotation of copper-activated pyrite and identify the mechanisms, which are involved in the interaction of sulphite both with the pyrite surface and collector (xanthate) species.

EXPERIMENTAL

MATERIALS AND REAGENTS

The pyrite sample was obtained from the Huanzala Mine, Peru. The elemental composition of pyrite analysed by ICP-MS (Inductively Coupled Plasma - Mass Spectroscopy) is shown in Table 1.

Table 1. Chemical assay of the pyrite sample

Mineral	Chemical elements present (Wt.%)								
	Fe	S	Ca	Mg	Mn	Si	Pb	Cu	Zn
Pyrite	44.93	53.51	0.45	0.08	0.02	0.69	0.02	0.13	0.18

All chemicals were of analytical grade. Cupric nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) was used to introduce copper ions during the conditioning time. Sodium isobutyl xanthate ($C_4H_9OCSSNa$, abbreviated as SIBX) and polypropylene oxide methanol (Dowfroth 250) were added in the experiments as a flotation collector and frother, respectively. The sulphite reagent used in the current studies as a depressant was sodium bisulphite ($NaHSO_3$). The slurry pH values of 7 and 9 were controlled using HCl solutions and a carbonate/bicarbonate buffer, respectively. Deionised water was used throughout the experimental work.

MINERAL GRINGING, CONDITIONING AND FLOTATION EXPERIMENTS

A known mass (50 grams) of pyrite was wet ground at 30% solids in a Fritsch ball centrifuge mill (200 ml volume) for 7 minutes. The d_{80} of the ground mineral was around 38 microns. After grinding, the slurry was washed from the mill into a 500 ml Gliwice flotation cell. The pulp was conditioned in 5 stages and four concentrates and the final tail were collected. The total time of flotation was 8 minutes. Wet and dry weights were measured for all flotation products. The pulp pH was kept constant during the flotation batch tests. Nitrogen (or air) purging was used throughout the study. The pulp Eh was measured using an Hg/Hg_2Cl_2 electrode. A summary of the experimental procedure is schematically shown in Figure 1.

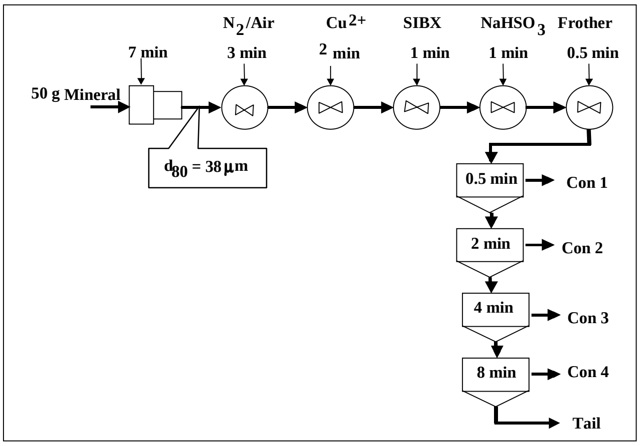

Fig. 1. Schematic presentation of the flotation procedure

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Fourier Transform Infrared spectra were obtained using a Nicolet Magna 750 spectrometer. The pyrite samples for FTIR analysis were prepared in a similar manner to the flotation experiments. The pulp pH was kept constant at around 7, while the slurry was nitrogen purged. After conditioning and filtration, the pyrite sample was placed in the cup of a Spectra Tech diffuse reflectance accessory apparatus. The contribution from pyrite was subtracted from all infrared spectra and the respective subtraction factors were close to 1.

UV-VISIBLE SPECTROSCOPY

A Varian CARY 5E spectrometer was used to determine the concentration of the xanthate remaining in solution before and after the addition of sodium bisulphite. Isobutyl xanthate was added to a 100 ml conditioning vessel containing deionised water that had been pre-purged with nitrogen prior to collector addition. The pH was adjusted to 7. The spectrum of xanthate was recorded within the range from 200 to 400 nm. Sodium bisulphite was then added and the absorption spectra were recorded as a function of time.

ION CHROMATOGRAPHY

A Water 431 conductivity detector was employed to determine sulphite stability and any adsorption onto pyrite in the presence and absence of adsorbed copper. Sulphur-oxy species in solution, i.e., sulphate (SO_4^{2-}) and sulphite (SO_3^{2-}), were measured using Waters Ion Chromatography Method with an IC-Pak A HC column. UV adsorption at 220 nm was used for the IC measurements. The pyrite samples were prepared in a similar way as in the flotation experiments shown in Figure 1. The pulp pH was kept constant at 9 using a carbonate/bicarbonate buffer and the slurry was nitrogen purged. After conditioning, the suspension was filtered to remove the solids and the amount of residual sulphite species was determined as a function of time.

RESULTS

FLOTATION STUDY

Figures 2 and 3 show the effect of sodium bisulphite on the flotation recovery of copper-activated pyrite pre-treated with isobutyl xanthate at pH 7 and 9, respectively. Table 2 presents the flotation data that have been analysed using the following first order kinetic equation (Lynch et. al 1981):

$$R = R_{max}\,(1 - e^{-kt}) \qquad (1)$$

where R is the percent of pyrite recovered at time t, R_{max} is the maximum flotation recovery at infinite time and k is the flotation rate constant (min^{-1}).

Under the experimental conditions studied (at pH 7 and 9), the effect of sodium bisulphite on the xanthate-induced flotation of copper-activated pyrite with nitrogen purging was found to be similar. In the presence of sulphite, the recovery of pyrite was reduced from 69.7% to 53.2% at pH 7 and from 69.3% to 57.7% at pH 9. During all flotation tests, a decrease in Eh of 40 mV was observed after sodium sulphite addition, which suggested a possible consumption of dissolved oxygen by sulphite ions.

Table 2. Maximum flotation recovery (R_{max}) and rate constant (k) of pyrite as a function of pulp pH

Experiment description	pH 7		pH 9	
	R_{max}	k	R_{max}	k
Pyrite only	15.2	0.30	18.0	0.30
Pyrite + Cu^{2+}	20.4	0.50	19.5	0.50
Pyrite + Cu^{2+} + SIBX	69.7	0.86	69.3	0.88
Pyrite + Cu^{2+} + SIBX + $NaHSO_3$	53.2	0.90	57.7	0.85

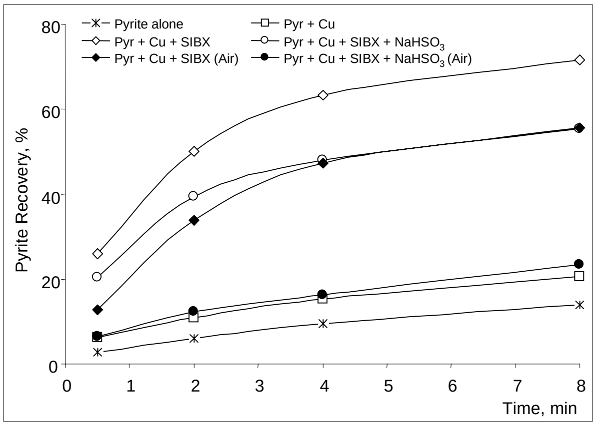

Fig. 2. Effect of sodium bisulphite on the flotation recovery of copper-activated pyrite pre-treated with isobutyl xanthate. All tests at pH 7, in nitrogen (empty symbols) and with air purging (filled symbols).

$[Cu(NO_3)_2] = 2.6 \times 10^{-4}$ mol dm^{-3};
[SIBX] $= 1.1 \times 10^{-4}$ mol dm^{-3};
$[NaHSO_3] = 1.9 \times 10^{-3}$ mol dm^{-3}

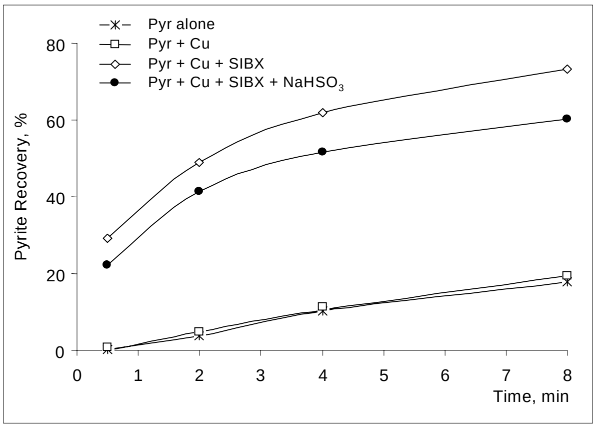

Fig. 3. Effect of sodium bisulphite on the flotation recovery of copper-activated pyrite pre-treated with isobutyl xanthate. All tests at pH 9, in nitrogen.

$[Cu(NO_3)_2] = 2.6 \times 10^{-4}$ mol dm^{-3};
[SIBX] $= 1.1 \times 10^{-4}$ mol dm^{-3};
$[NaHSO_3] = 1.9 \times 10^{-3}$ mol dm^{-3}

Additional flotation experiments were carried out with air purging to identify the effect of air on the xanthate-induced flotation of copper-activated pyrite either in the presence or absence of sodium bisulphite (at pH 7). In this case, the xanthate-induced flotation of copper-activated pyrite in an air atmosphere was lower compared to the same experiment with nitrogen purging. Recovery of pyrite was 71.8% in nitrogen and 55.6% in air. The combination of sodium bisulphite and air purging decreased the recovery of pyrite even further, from 55.6% to 32% (Figure 2).

Unless otherwise stated, pH 7 was chosen for additional spectroscopic studies conducted to identify the depression effects of sodium bisulphite on the xanthate-induced flotation of copper-activated pyrite.

FTIR STUDY

Figure 4 shows DRIFT FTIR spectra of adsorbed isobutyl xanthate on the surface of copper-activated pyrite at pH 7 with nitrogen purging in the absence and presence of sodium bisulphite.

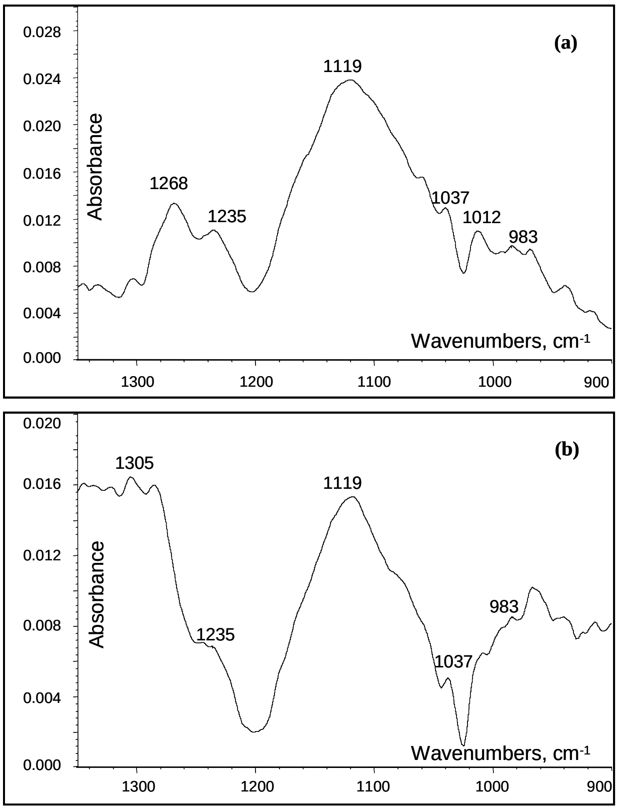

Fig. 4. Infrared spectra of isobutyl xanthate adsorbed on copper-activated pyrite conditioned at pH 7, in nitrogen: (a) in the absence of sodium bisulphite, (b) in the presence of $NaHSO_3$

$[Cu(NO_3)_2] = 1.0 \times 10^{-3}$ mol dm^{-3};
[SIBX] = 1.1×10^{-3} mol dm^{-3};
$[NaHSO_3] = 1.0 \times 10^{-2}$ mol dm^{-3}

The infrared bands observed in Figure 4a at 1230 - 1270 cm^{-1} are characteristic of dixanthogen (Poling 1961; Leppinen et. al 1988, 1989; Prestidge et. al 1993). The broad peak at 1120 cm^{-1} is due to incomplete subtraction of pyrite. In the presence of sodium bisulphite, the bands owing to isobutyl dixanthogen disappeared with loss of structure within the 1000 - 1100 cm^{-1} region (Figure 4b).

UV-VISIBLE STUDY

The adsorption spectra for the interaction of isobutyl xanthate with sodium bisulphite in solution have been recorded as a function of time at pH 7, as shown in Figures 5. It is clear that the initial xanthate concentration (peak at 301 nm) decreased with time, while at the same time, an adsorption band at 347 nm appeared (Figure 5). This suggested that an intermediate product of the xanthate decomposition, known as perxanthate, was formed (Yamamoto 1980). In approximately 15 minutes, xanthate was completely decomposed and virtually no xanthate or perxanthate were detected, as shown in Figure 6.

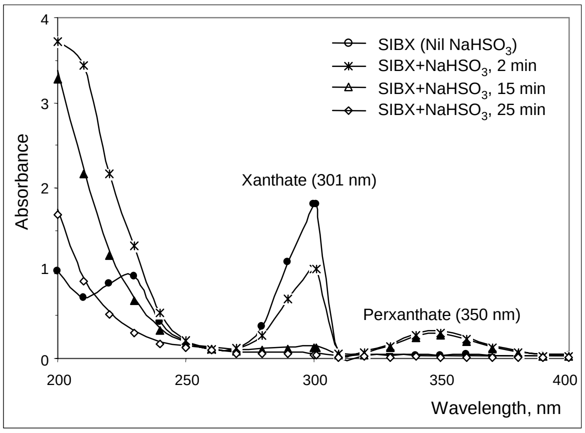

Fig. 5. UV spectra of isobutyl xanthate solution in the presence of sodium bisulphite as a function of time

All tests in the presence of 1.9 × 10^{-3} mol dm^{-3} NaHSO$_3$ added after pyrite conditioning with 1.1 × 10^{-4} mol dm^{-3} [SIBX], pH 7, in nitrogen

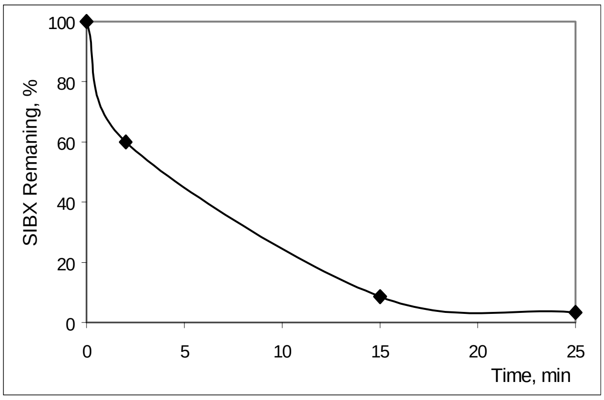

Fig. 6. Decomposition of sodium isobutyl xanthate (measured at 301 nm) in the presence of 1.9 × 10^{-3} mol dm^{-3} sodium bisulphite as a function of time, pH 7, in nitrogen

[SIBX] = 1.1 × 10^{-4} mol dm^{-3};
[NaHSO$_3$] = 1.9 × 10^{-3} mol dm^{-3}

ION CHROMATOGRAPHY STUDY

Figure 7 shows the stability of sulphite and adsorption onto pyrite in the presence and absence of copper ions at pH 9. The results are presented as sulphite (SO_3^{2-}) and sulphate (SO_4^{2-}) residual concentrations in solution versus time. In both cases, compared to their initial concentrations, the amount of sulphite remaining in solution decreases, while the amount of sulphate increases after 25 minutes of conditioning. However, in the presence of copper ions, less sulphite is detected in solution and the formation of sulphate is more rapid.

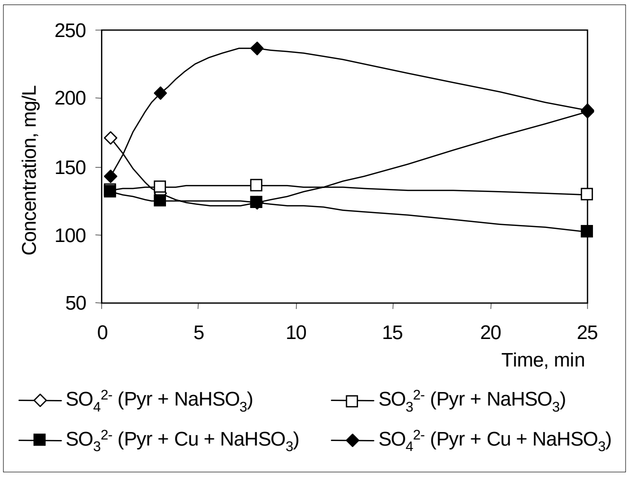

Fig. 7. Sulphite stability and adsorption onto pyrite measured by IC in the presence and absence of copper ions, at pH 9 (nitrogen purging)

$[Cu(NO_3)_2] = 2.6 \times 10^{-4}$ mol dm^{-3};
$[NaHSO_3] = 1.9 \times 10^{-3}$ mol dm^{-3}

DISCUSSION

Flotation data have shown that at pH 7 and 9 sodium bisulphite acts as a depressant for the xanthate-induced flotation of copper-activated pyrite with nitrogen or air purging. However, the depression effect of sulphite with air purging was found to be greater. It is possible that more oxidation products were formed on the pyrite surface with air purging, rendering it more hydrophilic (Figures 2). The depression of pyrite by sulphite may be explained by the results obtained from the spectroscopic and solution studies.

Infrared analysis has indicated that under the experimental conditions tested, isobutyl xanthate adsorbed on the surface of copper-activated pyrite in the form of dixanthogen. The addition of sodium bisulphite resulted in dixanthogen desorption (Figure 4). Since dixanthogen is the collector species responsible for pyrite flotation (Fuerstenau et. al 1968; Majima and Takeda 1968; Huiatt 1969; Huang and Miller 1978; Montalti 1994), desorption of dixanthogen from the surface can lead to the pyrite depression. Moreover, it was noticed that the introduction of sulphite decreased the pulp redox potential by 40 mV. Consequently, sulphite addition may also reduce the xanthate adsorption due to the lack of oxygen in solution, thus limiting dixanthogen formation (Miller 1970; Shen et. al 2001).

The results from UV-visible spectroscopy may further explain the decrease in the recovery of pyrite. It has been demonstrated that sulphite decomposed the xanthate ions in solution, as well as these present at the pyrite surface (Figures 5 and 6). Perxanthate was formed (at 350 nm) during the xanthate decomposition. A similar mechanism was proposed by Yamamoto (1980), who identified the products of the ethyl xanthate decomposition by sulphite as ethanol, thiosulphate and carbon dioxide.

Furthermore, the ion chromatography study has illustrated that less sulphite and more sulphate ions were found in solution when both sodium bisulphite and copper ions were present. It is likely that copper ions promoted the sulphite oxidation to sulphate. Sulphite ions also promoted the surface oxidation of copper-activated pyrite rendering it hydrophilic, thus reducing the floatability of pyrite particles (Figure 7). It was hence suggested that the consumption of sulphite from solution could be due to the sulphite adsorption on the mineral surface, sulphite oxidation to sulphate and surface precipitation of sulphite. Moreover, some additional sulphate in solution can be due to the direct oxidation of the pyrite surface (Hoyack at. al 1987).

Based on the results obtained in the current work, a compound effect of sulphite on the pyrite flotation has been suggested. It was found that under the studied experimental conditions, a combination of four mechanisms was responsible for the depression of the xanthate-induced flotation of copper-activated pyrite by sulphite, namely:

i) Xanthate decomposition in solution via perxanthate formation (Yamamoto 1980):

$$\mathrm{ROCSS^- + HSO_3^- + SO_3^{2-} + O_2 \rightarrow ROCSSO^- \rightarrow ROH + 2S_2O_3^{2-} + CO_2}$$

ii) Desorption of dixanthogen from the pyrite surface (Miller 1970):

$$\mathrm{Fe(C_4H_9OCSS)_2 + HSO_3^- \rightarrow 2C_4H_9OCSS^- + FeSO_3 + H^+}$$

iii) Consumption of dissolved oxygen by sulphite ions, accompanied by a drop of the pulp redox potential (Illyuvieva et. al 1984):

$$\mathrm{HSO_3^- + 1/2O_{2(aq)} \rightarrow SO_4^{2-} + H^+}$$

iv) Pyrite oxidation by sulphite ions, rendering the mineral surface hydrophilic (accompanied by an oxidation of thiosulphate to sulphate):

$$FeS_2 \rightarrow FeS + S^0 \text{ (Abramov and Avdohin 1997)}$$

$$S^0 + HSO_3^- \rightarrow S_2O_3^{2-} + H^+ \text{ (Li et. al 1995)}$$

CONCLUSION

Sulphite depressed the xanthate-induced flotation of copper-activated pyrite at pH 7 and 9. The depressant effect of sulphite ions can be improved using air purging instead of nitrogen. Spectroscopic and solution studies revealed that depression of the pyrite flotation was due to the sulphite interaction with the isobutyl xanthate in solution and its adsorbed state, as well as with the pyrite surface itself.

The specific effect of sulphite ions on the surface chemistry of copper-activated pyrite pre-treated with isobutyl xanthate will be further determined using XPS and ToF-SIMS analyses. These spectroscopic techniques will allow identifying the type and exposure of the surface species that may be responsible for the pyrite depression. This study is ongoing and the results obtained will be discussed in a future work.

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Khmeleva T.N., Skinner W., Beattie D.A., Georgiev T.V., *Wpływ siarczynu sodu na flotację pirytu aktywowanego miedzią z udziałem ksantogenianu,* Fizykochemiczne Problemy Mineralurgii, 36, (2002) 185-195 (jęz. ang.)

Do badania wpływu siarczynu sodowego na proces flotacji pirytu aktywowanego miedzią użuto szeregu technik badawczych. Ich zadaniem było wyjaśnienie mechanizmu oddziaływania siarczynu sodowego z kolektorem (ksantogenianem izobutylowym) oraz z powierzchnią pirytu. Odkryto, że siarczyn depresuje flotację pirytu aktywowanego miedzią przy udziale ksantogenianu w warunkach pH 7, przy przepływie azotu lub powietrza. Depresujący efekt był większy, gdy powietrze zostało użyte. Badania spektroskopowe wskazują, że siarczyn sodu reaguje z powierzchnią pirytu a także z izobutylowym ksantogenianem i to zarówno w roztworze jak i na powierzchni ciała stałego. Na tej podstawie zaproponowano mechanizm depresji aktywowanego pirytu przez siarczyn sodu. Wyniki badań sugerują, że zarówno dekompozycja ksantogenianu jak i desorpcja dwuksantogenu z powierzchni pirytu są czynnikami odpowiedzialnymi za depresowanie pirytu. Dodatkowo zaobserwowano powstawanie na powierzchni pirytu grup hydroksylowych, które dodatkowo depresowały piryt, powodując hydrofilizacje jego powierzchni i brak możliwości utworzenia trwałego agregatu z banieczką powietrza.