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ON THE INTERPRETATION OF THE XPS SPECTRA OF ADSORBED LAYERS OF FLOTATION COLLECTORS − ETHYL XANTHATE ON METALLIC LEAD

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Ethyl xanthate adsorption on metallic lead was studied by X-ray photoelectron spectroscopy (XPS) after treatment of lead sample at different potentials in aqueous $NaNO_3$ solutions containing ethyl xanthate. Continuous increase of the amount of ethyl xanthate species on the lead surface was observed as the potential was raised from –400 mV to –340 mV at the ethyl xanthate concentration of 10^{-4} M. At the potential of –400 mV and the concentration of 10^{-4} M the amount of xanthate at the surface was at the detection limit. Lead oxide and lead carbonate were found as the main oxidation products of metallic lead. Ethyl xanthate layer was found to decompose to sulfide like species in a few hours of excitation with monochromatic AlK_α radiation, if XPS measurement was done at room temperature. Cooling the sample with liquid nitrogen down to $T \approx 130$ K prevented the decomposition.

Key words: X-ray photoelectron spectroscopy, xanthate, surface adsorption, lead

INTRODUCTION

Lead is one of those base metals existing mainly in the form of sulfides in the earth's crust. Lead sulfide (PbS, galena) is separated from the ore using a flotation process, where the surfaces of finely ground sulfide particles are made hydrophobic by adding suitable surface active reagents (collectors) to the process solution. Xanthates are the most popular collector reagents and there are a lot of papers published in the literature where the interaction between xanthate species and the lead sulfide surface is studied using, for example, different electrochemical, infrared and surface spectroscopic techniques (XPS, STM, SIMS etc.).

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In many surface analytical techniques, like in XPS, the measurement is carried out in ultra high vacuum (UHV) causing some limitations and problems when phenomena occurring at solid-liquid interfaces need to be studied. These difficulties and methods for minimizing the problems have been discussed several times in the literature (Kartio et al., 1992; McCarron et al., 1990; Smart, 1991). General conclusion is that to get relevant information with XPS, sample preparation procedures have to be carefully planned and often sample need to be cooled with liquid nitrogen even before introduction into the electron spectrometer and kept cool also during the measurement. Using proper procedures, XPS and other surface sensitive UHV techniques can still give valuable information from collector adsorption and the composition of the mineral surfaces under different conditions.

It is widely accepted that at early stages of interaction xanthate is bonded to lead sites in PbS therefore suggesting this interaction to be of primary importance. Although xanthate sulfurs have slightly different binding energies than sulfurs in PbS, low amounts of adsorbed xanthate is quite difficult to separate in XPS spectra from strong sulfur signal originating from the PbS substrate.

These observations in mind, we considered interesting to study the interaction of ethyl xanthate on metallic lead with XPS thus avoiding the problem of large background sulfur signal, but leaving the possibility to investigate the sulfur-lead interaction. Furthermore, only a few earlier studies of xanthate interaction with metallic lead have been published, but none of them include any surface spectroscopic technique. Tolun and Kitchener (1964) published the first electrochemical results, where they made a surprising observation that lead electrode covered with xanthate remained hydrophilic, although for a long time lead xanthate has been known to render the galena surface hydrophobic. They proposed this hydrophilicity to be due to excess xanthate ions in a layer. Later Woods (1972) reported his first electrochemical work and then Woods et al. (1997) recorded voltammograms at pH 9.2 and pH 6.8 using different concentrations of ethyl xanthate (10^{-2}, 10^{-3} or 10^{-4} M). On the basis of those measurements they calculated the Frumkin type isotherms for the system.

Our goal was to observe directly with XPS the surface composition of lead surface treated with ethyl xanthate solution at different electrode potentials. Questions of the role of oxidation products for hydrophilicity of the lead electrode reacted with xanthate and possible differences in sulfur binding in the case of monolayer and multilayer coverage were also addressed.

EXPERIMENTAL

The Perkin-Elmer PHI 5400 spectrometer equipped with monochromatized AlK$_\alpha$ X-ray source was used. The binding energy (BE) scale of the spectrometer was calibrated with the Au4f$_{7/2}$ (BE = 84.0 eV) and Cu2p$_{3/2}$ (BE = 932.6 eV) lines. With this calibration the BE for the Pb4f$_{7/2}$ line in the sample of metallic lead, abraded at the ultra high vacuum (neither carbon nor oxygen emission lines were observable in the spectra) was 136.9 eV. Unless otherwise stated the spectra were recorded at the 45^o take-off-angle. A slice of metallic lead (Goodfellow) was cut from the rod having the purity of 99.95% and used as an electrode. All reagents used were of “analytical reagent“ grade. Water from Elgastat UHQ MKII apparatus (resistivity 18 MΩ) was used in experiments and to prepare the solutions. Ag/AgCl/saturated KCl electrode was used as a reference, but all potentials are, however, reported versus standard hydrogen electrode (SHE) assuming that Ag/AgCl/saturated KCl electrode has the potential +0.2 V versus SHE. Platinum wire was used as a counter electrode. The base electrolyte was 0.1 mol/dm^3 $NaNO_3$ and the solutions were purged from oxygen by bubbling with 99.999% nitrogen gas before each electrochemical experiment. The fresh surface of the lead electrode was obtained by cutting with a steel blade. The electrode was first polarized to the potential –0.8 V in pure base electrolyte to reduce the oxidation products from the surface, then xanthate was added, the solution stirred quickly (the potential kept at -0.8 V all the time) and the sample immediately polarized to the required potential. Electrode was kept at that potential for 1 minute, withdrawn, rinsed with water and introduced to the spectrometer immediately. Sample pre-cooling was used (Kartio et al., 1992) and the spectra were recorded at sample temperature 130 K. For selected samples, the sample was let to warm up to room temperature after the acquisition and the spectrum re-measured to check the stability of the reaction product.

RESULTS AND DISCUSSION

METALLIC LEAD TREATED IN AQUEOUS SOLUTION WITHOUT XANTHATE

When metallic lead was treated in an electrolyte solution containing no xanthate at E_h = -410 mV, the surface was covered by a thick layer of oxidation products most of them probably formed during the transfer of lead sample from the electrochemical cell into the electron spectrometer. Although the transfer time was of the order of one minute, active metals like lead oxidizes immediately in contact with air (Nowak et al. 2000). According to O1s and C1s spectra, main species on a surface were lead oxide and lead carbonate. Only about 5 % of lead signal were from metallic lead suggesting the oxidized layer thickness of the order of 5 nm. This layer, especially the lead carbonate (lead oxide is a semiconductor) is also a poor electrical conductor causing surface charging observed in all samples. The amount of charging was estimated using C1s contamination line at 285.0 eV as a reference and it varied between 0.3 eV and 0.8 eV, the largest value found in this sample which was not treated with xanthate.

After charging correction of 0.8 eV (Table I), O1s binding energy 529.2 eV was determined which is typical for oxygen in lead oxide and binding energy 530.9 eV was found for lead carbonate. Carbon emission at 288.7 eV confirmed the existence of carbonate. By comparing the intensities of the carbonate peaks (288.7 eV and 530.9 eV) corrected with elemental sensitivity factors, very good agreement was found with the lead carbonate stoichiometry. The broad O1s signal fitted at 532.7 eV (16 % of total oxygen) can be interpreted to be due to lead hydroxide, adsorbed water or some organic species as discussed in the literature (Nowak et al., 2000).

Table 1. Binding energies of measured photoemission lines from samples treated at different potentials in aqueous ethyl xanthate solutions at pH 6.7. Relative intensities of fitted components for each emission are given in parenthesis. All binding energies are corrected in respect to the measured value 136.9 eV for Pb4f$_{7/2}$ binding energy in metallic lead

Xanthate conc. mol/l	Potential E_h /mV	Binding energy / eV				
		C1s	O1s	S2p	S2s	Pb4f$_{7/2}$
10^{-4}	-340	289.6 (2) 287.7 (16) 286.6 (13) 285.3 (69)	533.7 (70) 531.8 (17) 529.9 (13)	162.5	226.8	136.9 (5) 138.4 (95)
10^{-4}	- 360	289.7 (2) 287.9 (16) 286.7 (28) 285.5 (54)	533.9 (61) 531.8 (21) 530.0 (18)	162.7	226.9	136.9 (4) 138.5 (96)
10^{-4}	- 380	289.1 (8) 287.8 (8) 286.9 (14) 285.6 (70)	533.9 (20) 531.4 (49) 529.7 (31)	162.6	226.9	136.9 (15) 138.3 (85)
10^{-4}	- 400	289.1 (9) 286.5 (13) 285.7 (78)	533.8 (3) 531.9 (71) 530.1 (26)	(162.5)	- (too weak)	136.9 (4) 138.5 (96)
10^{-3}	-410	288.4 (6) 287.8 (19) 286.5 (27) 285.3 (58)	533.8 (59) (38) 530.0 (3)	162.5	226.8	136.9 (2) 138.6 (98)
0	- 610	289.4 (9) 286.6 (22) 285.8 (69)	533.5 (17) 531.7 (54) 530.0 (29)	-	-	136.9 (4) 138.5 (96)

Considering the lead oxidation products, lead hydroxide seems therefore be of minor importance, the main products being oxide (62 % of oxidized lead) and carbonate (38 % of oxidized lead). In the C1s spectrum the main component at 285.0 eV was due to hydrocarbon type contamination. Small amount of carbon-oxygen species was also detected in the region of 286 eV. This first experiment is not very informative, because the amount and type of oxidation species present when sample was still in electrolyte solution could not be concluded. However, this experiment can be used to estimate the uniformity and stability of xanthate covered surface against air oxidation by comparing the results with surface compositions of samples treated in xanthate solutions.

METALLIC LEAD TREATED IN AQUEOUS SOLUTION CONTAINING 10^{-4} M ETHYL XANTHATE

Four samples treated at potentials -400 mV, -380 mV, -360 mV and -340 mV and ethyl xanthate concentration 10^{-4} M were prepared. All samples were cooled inside the spectrometer to avoid decomposition of surface species during acquisition, which was observed when the samples were measured at room temperature. The decomposition will be discussed in more detail later in this paper. Only traces of xanthate (at the limit of detectability) were observed at potential of -400 mV but the amount of non-xanthate oxygen was almost the same as in the case of the sample treated in pure base electrolyte. This is in disagreement with the results by Woods et al (1997) who observed the chemisorption prewave in the region from -670 mV to -460 mV and concluded the formation of a full xanthate monolayer already at approximately -460 mV using xanthate concentration 10^{-4} M. The monolayer of chemisorbed xanthate on metal surface should be easily detected with XPS. This discrepancy may be explained if one assumes that xanthate species are not very strongly bonded to lead and in air are replaced or buried by such oxidation products as carbonate or oxide. Another possibility is that the end of the prewave does not indicate the formation of a full monolayer, but only some completion of the most favorable adsorption sites and therefore the potential -460 mV represents still under monolayer situation.

All spectra measured at different potentials were curve fitted to determine different chemical states of each element. Summary of the results is presented in Table 1, where all binding energies are given without charge correction, but corrected against the Pb4f$_{7/2}$ binding energy of 136.9 eV in metallic lead. Charge correction with C1s contamination line is not automatically done, because there seems to be slight differences in charging between different species even in the same sample depending on the distribution and amount of different species in each case. By looking the BE of C1s contamination line, the charging decreases when xanthate treatment potential increases. This is an indication that larger amount of xanthate adsorbed at higher potentials reduces the oxidation and therefore works like an oxidation inhibitor as shown in Fig. 1 (curve A), where intensity ratio O_{ox}/Pb (O_{ox} is the total O1s intensity of oxidation products i.e. oxide+carbonate) is plotted at different potentials. Especially the formation of highly insulating carbonates is decreased as concluded from the C1s spectra of the –340 mV and –360 mV samples where carbonate component is hardly visible and shifted to higher binding energies as observed earlier at the early stages of oxidation (Laajalehto et al., 1993). When the amount of xanthate is lower on the surface, the carbonate signal intensity is significantly enhanced and its binding energy decreased.

Ethyl xanthate can be easily identified according to characteristic binding energies of S2p, S2s and O1s emissions for which we obtained average values of 162.2 eV, 226.4 eV and 533.4 eV after charge correction, respectively. The values obtained are in good agreement with earlier studies of ethyl xanthate adsorption on PbS and the values presented for $Pb(EX)_2$ (Laajalehto et al., 1993). The relative amount of xanthate at different potentials was estimated using the measured intensity ratios O_{xant}/Pb (Fig. 1, curve B) and S/Pb (Fig. 1, curve C). They show continuous increase of the ratios as a function of the potential. The amount of xanthate at potential –340 mV represents definitely a multilayer situation.

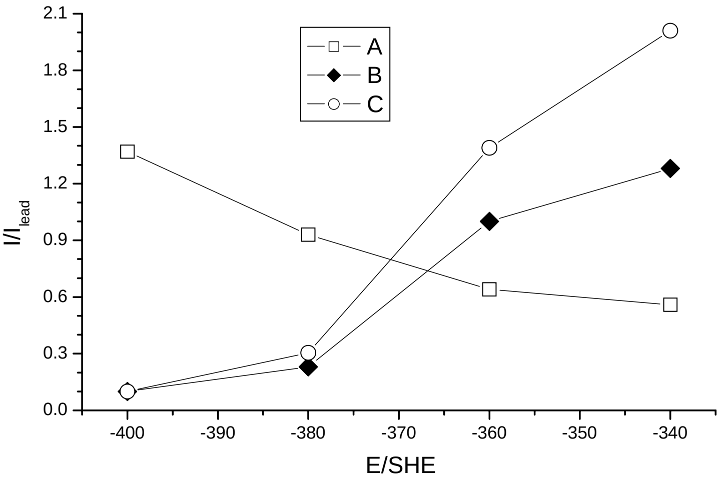

Fig. 1. Ratio of the intensity of the particular emissions to the total emission of lead for samples treated at different potentials and at the 10^{-4} M xanthate concentration. A – oxygen in oxidation products, B – xanthate oxygen, C – xanthate sulphur

In O1s spectra after xanthate treatment, three components are observed. In addition to xanthate oxygen at BE 533.4 eV, carbonate and oxide species are also detected in all spectra. Because metallic lead was first reduced at –800 mV before xanthate was added and then the potential increased to the final value, it can be assumed that lead surface was free of oxidation products in solution. Therefore most of the oxidation products were formed in air after the sample was taken out from the solution and dried, and before insertion to the spectrometer. This indicates that xanthate layer formed in solution is either not uniform or it does not totally protect the lead surface against air oxidation.

For a sample treated at –410 mV and ethyl xanthate concentration 10^{-3} M, O1s spectra at different electron take-off angles from 20° to 75° were recorded giving information about the layer structure on the surface region. These measurements show that on average carbonate species are on the top of xanthate therefore suggesting that they have formed in air by reaction of carbon dioxide with lead xanthate or lead diffused from the substrate. Removal of surface xanthate by carbonates cannot be excluded either.

Important observation is that sulfur binding energy does not significantly change (all changes are within 0.2 eV) when the conditions are changed from those for which monolayer formation might be expected to formation of lead xanthate. This supports our earlier measurements with bulk $Pb(EX)_2$ where binding energy 162.2 eV was found (Laajalehto et al., 1993) and the SR-XPS measurements of a monolayer coverage of xanthate on PbS (Kartio et al., 1999), where S2p binding energy 162.0 eV was reported. Much larger shift, about 1 eV, proposed earlier by Buckley and Woods, is not consistent with our findings in this work and in the papers referred above.

One sample with higher ethyl xanthate concentration 10^{-3} M was also prepared at potential -410 mV i.e. at potential where xanthate was not observed with concentration 10^{-4} M. The measured spectra are very similar to those obtained at –340 mV and –360 mV and with concentration 10^{-4} M. This confirms the electrochemical nature of the process, which proposes that one order of magnitude increase in xanthate concentration would shift the reaction potential by 60 mV.

STABILITY OF THE XANTHATE LAYER IN EXPERIMENTAL CONDITIONS

It has been well documented that two types of damage can occur in XPS measurements. Firstly, in ultra high vacuum weakly bonded surface species can detach from the surface already during pumping down the sample chamber and those species will therefore be not detected in the subsequent XPS measurements. Well known flotation related system of this is the observation of physisorbed dixanthogen on pyrite or metallic gold surfaces, which is only possible using a specially designed pre-cooling method (Kartio et al., 1992). Secondly, X-ray radiation used to excite the photoelectron spectra can directly or indirectly cause decomposition or evaporation of surface species. It was observed by Johansson et al. (1986) that using a monochromatized AlK_{α} radiation instead of non-monochromatized MgK_{α} radiation prevented the decomposition and evaporation of xanthate bonded to metallic copper. It was also observed that cooling the sample during the measurement with liquid nitrogen significantly decreased the decomposition also in the case of non-monochromatized MgK_{α} radiation.

Although monochromatized AlK_{α} radiation was used in all measurements in this work, decomposition of xanthate was observed if measurements were done at room temperature. In Fig. 2, four sulfur 2p spectra are presented of the same sample originally treated in 10^{-3} xanthate solution at potential –340 mV. First measurement was done by keeping the sample at low temperature (130 K, spectrum a) and the spectrum shows the characteristic 2p doublet structure for a single chemical state of xanthate sulfur. Spectrum b was measured immediately after warming up the sample to room temperature corresponding to only 11 min irradiation time as warm, which was needed to record the spectrum. A weak shoulder at lower binding energy side of the xanthate peak is already visible indicating a new chemical state of sulfur. When irradiation time increased (3h in spectrum c and 10 h in spectrum d), the structure at about 160.7 eV (after charging correction) continuously increased in intensity suggesting xanthate decomposition to lead sulfide like species at room temperature. Formation of PbS type species on the surface is further supported by the observation that Pb4f emission from oxidation products is shifted ≈0.3 eV towards lower binding energy. This shift is caused by the decrease of lead xanthate signal at higher BE side of that emission line and simultaneous increase in PbS type intensity at the other side of the peak. No separate components can be resolved, because all these three chemical states (lead xanthate, lead carbonate/oxide and lead sulfide) are within 1 eV. By comparing the sulfur and oxygen intensities for cool and warm sample, it is plausible to assume that the bond between CS_2 group and oxygen is broken and the hydrocarbon part, including the oxygen atom, is evaporated.

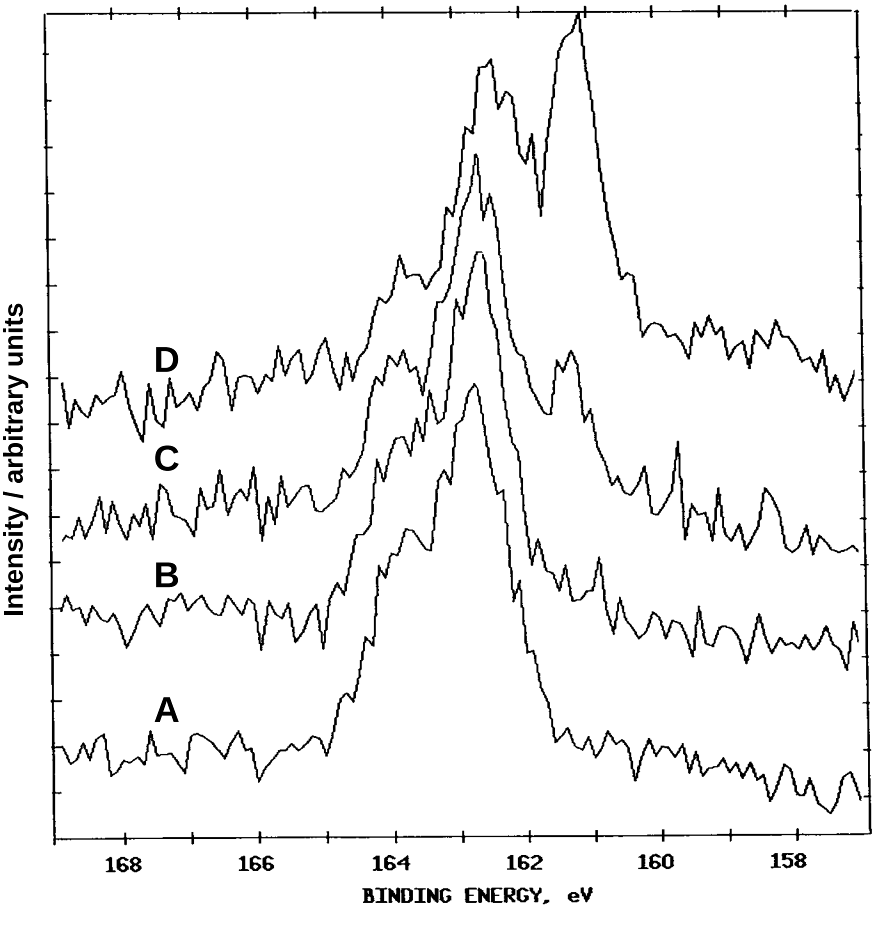

Fig. 2. S2p emission line for the sample treated at the potential of –410 mV in 10^{-3} M xanthate solution. A – measured cool, B – just after warming to room temperature, C – after 3 hours of irradiation, D – after 10 hours of irradiation

Decomposition has also been observed for adsorbed layer of ethyl xanthate on PbS surface after excitation with intensive synchrotron radiation (Kartio et al., 1999). It is interesting to note that decomposition products on PbS surface were identified as polysulfide type sulfur species having higher binding energy than xanthate sulfur whereas in metallic lead, decomposition product is sulfide type. Probable reason for this is that in the case of metallic lead there are lead atoms easily available to form sulfide, which suggests that decomposition takes place on the boundary between metal and xanthate. On PbS surface lead atoms are not so active and sulfur atoms start to form chain-like structures.

The reason for xanthate decomposition is evidently the high photoelectron and secondary electron yield in metallic lead. To explain the more serious damage observed with lead compared to that with copper substrate, the following phenomena can be considered: 1) the total cross section of photoelectron emission for AlK_α excitation in lead is much higher than in copper and, 2) the kinetic energy of photoelectrons in the most probable photoemission in lead (4f emission, $E_K \approx 1300$ eV) is significantly higher than for corresponding emission in copper (2p emission, $E_K \approx 550$ eV). Because of the about 50 % lower atomic density of lead atoms in PbS and much lower photoemission cross-section for S, the decomposition probability is much lower and practically not detected with conventional AlK_α radiation at room temperature. Our measurements show, however, that practically all damage also in this case can be avoided by using sample cooling during the excitation. No pre-cooling is needed because xanthate is either chemisorbed or lead xanthate is formed both species being not volatile and therefore not affected by the vacuum itself.

CONCLUSIONS

Xanthate adsorption on metallic lead was found to be potential dependant in a studied potential region between –410 mV and –340 mV. Using ethyl xanthate concentration 10^{-4} M, negligible amount of xanthate was detected at –400 mV, however the amount of xanthate grew with potential sharply attaining multilayer coverage at higher potentials. The binding energy of S2p electrons was within 0.2 eV at all xanthate coverage indicating that there is only a slight difference in sulfur chemical state. The adsorbed xanthate was always accompanied by lead oxidation products. Evidently the xanthate overlayer is either not compact or it is weekly bound to the surface and the surface covered by xanthate, either at monolayer or multilayer coverage may still react with atmospheric gases. This explains why Tolun and Kitchener found the surface of xanthate-covered lead hydrophilic. To avoid radiation damage during the XPS measurement, sample need to be cooled with liquid nitrogen. If the sample is at room temperature during the measurement, xanthate is decomposed to lead sulfide like species. Decomposition is caused by large amount of energetic photoelectrons from lead excited by AlK_α radiation and their interaction with adsorbed layer.

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REFERENCES

JOHANSSON, L.S., JUHANOJA, J., LAAJALEHTO, K., SUONINEN, E. and MIELCZARSKI, J., 1986. *XPS studies of xanthate adsorption on metals and sulfides,* Surf. Interface Anal., 18: 501-505.

KARTIO, I., LAAJALEHTO, K., SUONINEN, E., KARTHE, S. and SZARGAN, R., 1992. *Technique for XPS measurements of volatile adsorbed layers: application to studies of sulphide flotation*, Surf. Interface Sci., 18: 807-810.

KARTIO, I., LAAJALEHTO, K. and SUONINEN, E., 1999. *Characterization of the ethyl xanthate adsorption layer on galena (PbS) by synchrotron radiation excited photoelectron spectroscopy*, Colloids Surf. A, 154: 97-101.

LAAJALEHTO, K., NOWAK, P. and SUONINEN, E., 1993. *On the XPS and IR identification of the products of xanthate sorption at the surface of galena,* Int. J. Miner. Process., 37: 123-147.

LAAJALEHTO, K., SMART, R.St.C, RALSTON, J. and SUONINEN, E., 1993. *STM and XPS investigation of reaction of galena in air,* Appl. Surf. Sci., 64: 29-39.

McCARRON, J.J., WALKER, G.W. and BUCKLEY, A.N., 1990. *An X-ray photoelectron spectroscopic investigations of chalcopyrite and pyrite surfaces after conditioning in sodium sulfide solutions,* Int. J. Miner. Process., 30: 1-16.

NOWAK, P., LAAJALEHTO, K. and KARTIO, I., 2000. *A flotation related X-ray photoelectron spectroscopic study of the oxidation of galena surface,* Colloids Surf. A, 161: 447-460.

SMART, R.St.C., 1991. *Surface layers in base metal sulphide flotation, Minerals Engineering*, 4: 891-909.

TOLUN, R. and KITCHENER, A., 1964. *Electrochemical study of the galena-xanthate-oxygen flotation system,* Trans. IMM, 73: 313-322.

WOODS, R., 1972. *The anodic oxidation of ethyl xanthate on metal and galena electrodes,* Aust. J. Chem., 25:2329-2335.

WOODS, R., CHEN, Z. and YOON, R.-H., 1997. *Isotherms for the chemisorption of ethyl xanthate on lead,* Int. J. Miner. Process., 50: 47-52.

Nowak P., Laajalehto K., *O interpretacji emisyjnych widm elektronowych (XPS) warstw adsorpcyjnych odczynników flotacyjnych – ksantogenian etylowy na powierzchni ołowi,* Physicochemical Problems of Mineral Processing, 41 (2007) 107-116 (w jęz. ang.).

Adsorpcję ksantogenianu etylowego na powierzchni metalicznego ołowiu z roztworów wodnych $NaNO_3$ badano metodą spektrometrii fotoelektronów generowanych promieniowaniem rentgenowskim (XPS, ESCA). W roztworze ksantogenianu o stężeniu 10^{-4} mol dm^{-3}, wraz ze wzrostem potencjału od wartości -400 mV do - 340 mV (względem standardowej elektrody wodorowej), ilość ksantogenianu na powierzchni wrasta od wartości znikomo małej (na pograniczu możliwości detekcji) do pokrycia wielowarstwowego. Widmo produktu sorpcji jest identyczne z widmem ksantogenianu ołowiu. We wszystkich widmach obserwowano produkty utlenienia ołowiu, produktu te zidentyfikowano jako mieszaninę węglanu i tlenku ołowiu (II), przy czym im wyższy potencjał polaryzacji próbki w roztworze ksantogenianu tym mniej produktów utlenienia obserwowano na powierzchni. Produkty te powstawały w wyniku utlenienia ołowiu w trakcie kontaktu próbki z powietrzem atmosferycznym podczas przenoszenia próbki z roztworu do spektrometru, co świadczy o tym, że powstająca warstwa produktu sorpcji ksantogenianu nie zabezpiecza powierzchni ołowiu przed utlenianiem. W wyniku naświetlania powierzchni promieniowaniem rentgenowskim w trakcie pomiaru, powstały na powierzchni ołowiu ksantogenian ołowiu rozkłada się do produktu, którego widmo jest identyczne z widmem siarczku ołowiu. Można temu zapobiec przeprowadzając pomiar w temperaturze ciekłego azotu.