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ETHYLXANTHATE ADSORPTION AND KINETICS OF ADSORPTION ON LEAD MODIFIED GALENA AND SPHALERITE UNDER FLOTATION CONDITIONS

The effect of lead ions on the galena and sphalerite surface properties, ethylxanthate adsorption and kinetics of ethylxanthate adsorption in alkaline medium were studied for the possible use of recycled flotation water. The flotation tests and the zeta-potential measurements were carried out and correlated with the results of the infrared attenuated total reflection spectrophotometry (ATR–IR) and UV data. Lead adsorbed on the galena or sphalerite surface as $Pb(OH)^+$ and less as Pb^{2+} reduces the collectorless galena floatability from pH 7 to 9.5, but has a strong activating effect on natural sphalerite floatability (in pH range 7.6–10.5). After collection of Pb-modified minerals with K-ethylxanthate both forms of lead ethylxanthate, monolayer Pb–EX (chemically adsorbed $(EX)^-$), and multilayer, physically adsorbed $Pb(EX)_2$, were detected on the mineral surfaces. Sphalerite floated nearly 100% in the examined pH range, but galena floated better only from pH 8 to 9.5 (85–95%). The main surface reaction in pH range 8–9.5 is probably the ion-exchange reaction $M–Pb–OH + (EX)^- = M–Pb–EX + (OH)^-$ (M – mineral), which contributes to the chemical adsorption of $(EX)^-$ as monolayer –Pb–EX, on the surface of either of the mineral. The reaction between Pb-treated mineral and $(EX)^-$ ion is the reaction of pseudo-first order (on Pb-modified galena – rate constant is $k = 0.711\ \text{min}^{-1}$; on Pb-modified sphalerite $k = 0.102\ \text{min}^{-1}$).

INTRODUCTION

With the view to avoiding additional impact on the environment and reducing the fresh water demand the interest has grown in the use of recycled industrial waste water in mineral processing. Recycled effluent from flotation plants, which contains various ions, is expected to have significant effects on the surface characteristics, floatability and selectivity of minerals.

Galena is known to float well with xanthates (Fuerstenau M.C., 1982; Poling and Leja, 1963; Woods, 1971) but the short-chain xanthate homologues have a low ability to collect sphalerite (Fuerstenau, D.W. 1982; Mielczarski, 1986). Some investigators have studied the copper-ion effect on xanthate adsorption on sphalerite (Finkelstein and Allison, 1976; Termes and Richardson, 1986; Popov and Vučinić, 1990; Vučinić

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and Popov, 1995a) and galena (Popov and Vučinić, 1989; Vučinić and Popov, 1995a). Also, the chemical effects of Pb(II) on flotation and surface characteristics of sphalerite (Popov et al., 1989; Vučinić and Popov, 1995b) or synthetic ZnS (Ralston and Healy, 1980; Ralston et al., 1980) and on galena (Vučinić, 1992) were reported earlier, but the mechanisms have not been completely understood.

The purpose of this work was to study the effect of lead dissolved in a solution on the surfaces of galena and sphalerite, ethylxanthate adsorption and kinetics of ethylxanthate adsorption on minerals in alkaline medium. As Pb(II) may be present in the pulp during Pb–Zn flotation as a dissolved mineral constituent, added reagent (Pb-acetate), or in the recycled flotation water, it is very important to know how lead reacts with mineral surfaces and whether it influences the Zn- or Pb-concentrate qualities. The changes taking place in the mineral surfaces were identified by infrared attenuated total reflection spectrophotometry (ATR–IR), and correlated with UV data, flotation tests and zeta-potential measurements.

EXPERIMENTAL

Natural galena and sphalerite were manually selected and ground in an agate mortar. The fractions of –147 + 74 μm for galena and –208 +104 μm for sphalerite were used in flotation tests. For ATR–IR and zeta-potential measurements the grinding time was a few hours to obtain very fine powder. The specific areas of minerals were determined on a Culter Counter Model D Industrial (galena 4.00 m^2/g, sphalerite 2.97 m^2/g). Mineral samples were stored in a vacuum desiccator.

Chemical analysis showed that galena contained Pb 85.6% and S 13.7%. The characterization of sphalerite is given in Table 1.

Table 1. Chemical analysis of sphalerite

wt %		ppm*						
Zn 53.12	Fe 13.01	Pb 250	Cu 85	Cd 1520	Mn 4670	Cr 10	Ni 13	Sn 10

*Spectrochemical analysis

The pH values were adjusted using HCl and NaOH. Pb-acetate and Pb-nitrate were added in order to introduce lead ions into the mineral suspensions. $NaNO_3$ was used to adjust ionic strength in zeta-potential measurements. All the reagents were of p.a. grade. Commercial-grade potassium-ethylxanthate (KEX) was purified by multiple recrystallization from acetone.

Flotation tests were conducted in a modified Hallimond tube. One gram of the mineral in 0.1 dm^3 of the solution was conditioned at desired pH for three minutes after each reagent addition, then floated for three minutes at an air flow rate of 0.01 dm^3 per minute.

Zeta-potential measurements were taken on a Riddick Zeta-meter, using microelectrophoretic technique. A mineral suspension was stirred for 3 min after each addition of the reagents, and then the electrophoretic mobility was detected.

Reflection infrared spectra were recorded using a Perkin Elmer infrared spectrophotometer (type 397) with a Perkin Elmer ATR-attachment. The mineral suspension (0.250 g of the mineral and 0.025 dm^3 of distilled water with adjusted pH) was stirred with the selected reagent (Pb-acetate for 15 min., KEX for 15 min.). The solution of Pb-acetate was always decanted before KEX addition to prevent formation of precipitate in the bulk of the solution. After decantation of the KEX solution the sedimented mineral was placed in the germanium reflection element and IR spectra were recorded. The decanted collector solution was used in the UV analysis of the ethylxanthate concentration (λ_{EX} = 301 nm), by a Specord UV VIS spectrometer (Carl Zeiss Jena, G.D.R.). The amount of ethylxanthate abstracted was determined from the difference between initial (c_0) and final EX^- concentration (c_{EX}). The surface ethylxanthate coverage, θ, was calculated by taking into account a value of 0.288 nm^2 for the cross-sectional area of xanthate adsorbed on solid (Kakovsky, 1957). Kinetic studies of ethylxanthate adsorption were conducted on galena and sphalerite Pb-treated for 15 minutes.

RESULTS AND DISCUSSION

The collectorless floatabilities of galena and sphalerite in alkaline pH range are shown in figure 1, curve 1 and figure 2, curve 1, respectively. The flotation recovery of galena was high, about 70–80% (Fig. 1, curve l). Many authors agree that the level of the surface oxidation of sulphide minerals determines the level of the surface hydrophobicity or hydrophilicity. Metal-deficient sulphide surfaces (Buckley and Woods, 1984a; Buckley and Woods, 1984b; Buckley et al., 1985;) and elemental sulphur (Gardner and Woods, 1979; Hayes and Ralston, 1988) are proposed as the hydrophobic surface species responsible for good natural floatability. As elemental sulphur is unstable in alkaline pH solution (Ralston et al., 1981), the natural hydrophobicity of galena may be explained by the formation of a lead-deficient, hydrophobic sulphur-rich localized environment, $Pb_{1-x}S$, during the anodic oxidation reaction at the surface, coupled with cathodic reduction of atmospheric oxygen (Buckley and Woods, 1984a; Buckley and Woods, 1984b; Buckley et al., 1985; Hayes and Ralston, 1988) :

$$PbS + xH_2O = Pb_{1-x}S + xPbOH^+ + xH^+ + 2xe \qquad (1)$$

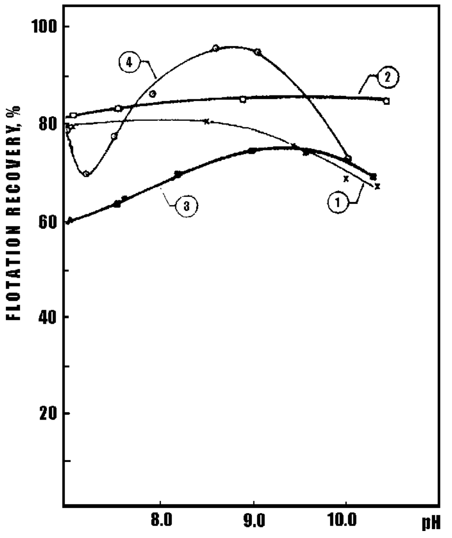

Fig. 1. Flotation recovery of galena as a function of pH, in presence of: 1) no reagents; 2) $3\cdot10^{-5}$ mol·dm^{-3} KEX; 3) $1.5\cdot10^{-5}$ mol·dm^{-3} Pb-acetate; 4) Pb-acetate and KEX

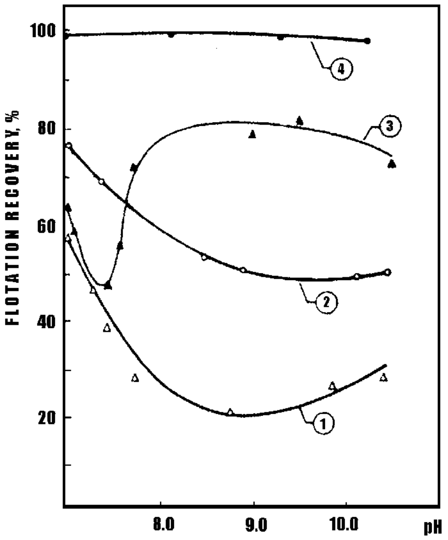

Fig. 2. Flotation recovery of sphalerite as a function of pH, in presence of: 1) no reagents; 2) $3\cdot10^{-5}$ mol·dm^{-3} KEX; 3) $1.5\cdot10^{-5}$ mol·dm^{-3} Pb-acetate; 4) Pb-acetate and KEX

$$\tfrac{1}{2}O_2 + xH_2O + 2xe = 2x(OH)^- \qquad (2)$$

However, the tested sphalerite had very poor natural floatability (Fig. 2, curve 1). Many investigators have noted that the oxidation process at the sphalerite surface is slow in air or an alkaline solution (Brion, 1980; Buckley et al., 1989). As the sphalerite used in this study contained about 13% Fe(II) in the crystal lattice and according to the mechanism of Buckley and Woods for ZnS (Buckley and Woods, 1984b), we presumed that the first stage of surface oxidation for our sample (Zn,Fe)S in natural or weakly alkaline solution, coupled with cathodic reduction of atmospheric oxygen, is the formation of hydrophobic zinc, iron-deficient sites and oxides:

$$(Zn,Fe)S + (x + y)H_2O = (Zn_{1-x},Fe_{1-y})S + xZnO + yFeO + 2(x + y)H^+ + 2(x + y)e \qquad (3)$$

$$1/2(x + y)O_2 + (x + y)H_2O + 2(x + y) = 2(x + y)OH^- \qquad (4)$$

Hydrophilic iron-oxygen and zinc-oxygen (or Zn and Fe hydroxides formed at high pH) are probably stronger bound in the electrical double layer of sphalerite, which may be the explanation for the obtained results of the low floatability (Fig. 2, curve 1). Also, hydrolysis of the surface metal-ions from the mineral lattice may result in the surface sites of –Pb–OH on galena or –Zn–OH and –Fe–OH on sphalerite. It is generally known that the hydrolysis of Zn(II) (Finkelstein an Allison, 1976; Ralston and Healy, 1980) and Fe(II) (Fuerstenau and Fuerstenau, 1982) in solution takes place at a lower pH than the hydrolysis of Pb(II) (Ralston and Healy, 1980; Fuerstenau and Palmer, 1976) and analogously, a higher surface concentration of –Zn–OH and –Fe–OH sites could be expected on sphalerite in a weakly alkaline medium than of –Pb–OH on that of galena. Due to surface centres, –Zn–OH and –Fe–OH contribute more to the hydrophilicity of sphalerite than –Pb–OH to galena. Also, the formation of surface sites (–MOH and –S– types) can be explained by hydrating mechanism for hydrous metal sulphide PbS and ZnS, proposed by Sun (1991). It has been deduced from the above considerations that at least four different surface centres on galena (Fig. 3a) and six on sphalerite can be formed (Fig. 3b).

The ethylxanthate anions $(EX)^-$ present in the mineral suspension induced a rise in the floatability (hydrophobicity) of both minerals (Fig. 1, curve 2 and Fig. 2, curve 2).

Lead ions, added in the mineral suspension, led to smaller flotation recovery of galena from pH 7 to 9.5 (Fig. 1, curve 3), but sphalerite flotation was activated above pH 7.6 (Fig. 2, curve 3), compared with their natural floatability (Fig. 1, curve 1 and Fig. 2, curve 1).

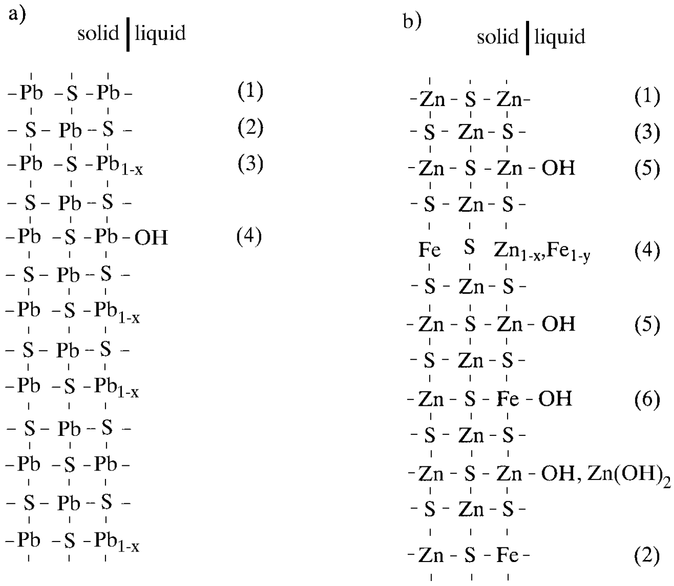

Fig. 3. Possible structure of the surface in an alkaline medium for:
a) galena; b) sphalerite

When KEX was used as a collector, the Pb-treated sphalerite floated nearly 100% (Fig. 2, curve 4). Under the same conditions, a better flotation recovery of Pb-treated galena was observed only in the pH range from 8.0 to 9.5 (85–95%, Fig. 1, curve 4).

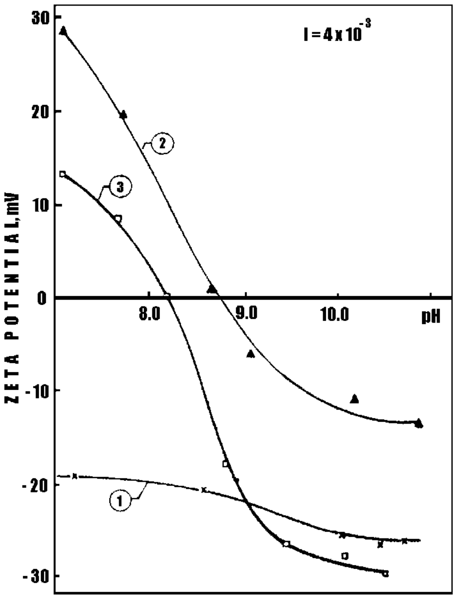

Fig. 4. Zeta-potential of galena as a function of pH in the presence of: 1) no reagents; 2) $5{\cdot}10^{-4}$ mol·dm^{-3} Pb-nitrate; 3) Pb-nitrate and $1.5{\cdot}10^{-4}$ mol·dm^{-3} KEX

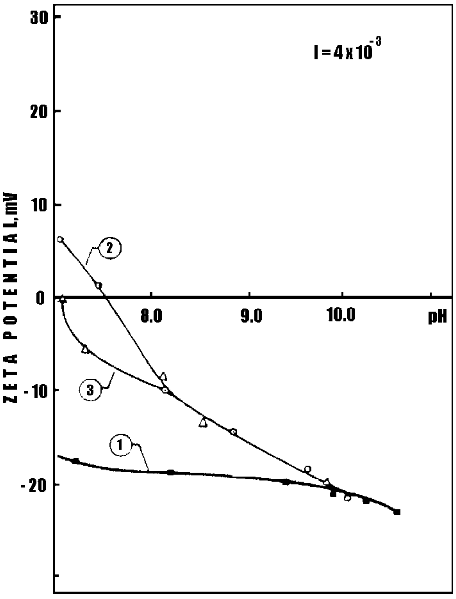

Fig. 5. Zeta-potential of sphalerite as a function of pH, in the presence of: 1) no reagents; 2) $5{\cdot}10^{-4}$ mol·dm^{-3} Pb-nitrate; 3) Pb-nitrate and $1.5{\cdot}10^{-4}$ mol·dm^{-3} KEX

According to the distribution diagram for lead (Ralston and Healy, 1980; Fuerstenau and Palmer, 1976), in alkaline medium (pH = 7–10) the dominant lead species in the solution are monoxydroxy complex ions $Pb(OH)^+$ and less Pb^{2+} ions. The effect of Pb(II) on minerals can be explained by the chemical adsorption of lead cations, $Pb(OH)^+$ and less Pb^{2+}, which was also confirmed by zeta-potential data (Fig. 4, compare curves 1 and 2; Fig. 5, compare curves 1 and 2). Consequently, the adsorbed lead cations on sphalerite surface relatively reduce the amount of the surface zinc and iron oxides or hydroxides (reactions 3 and 4, Fig. 3b), so that the surface becomes relatively less hydrophilic and sphalerite floats better. In the flotation experiment (Fig. 2, curve 3) one observes an increase of the flotation recovery of Pb-treated sphalerite, corresponding to $pH_{i.e.p.}$ = 7.5 (Fig. 5, curve 2). But $Pb(OH)^+$ adsorbed on galena diminishes its natural floatability as hydrolyzed cations fill up the lead-deficient sites, $Pb_{1-x}S$ (Fig. 3a, site 3), giving rise to hydrophilicity of the surface. The active surface sites for adsorption of lead cations in the Stern layer of the electrical double layer of minerals are metal-deficient centres, $Pb_{1-x}S$ and $Zn_{1-x}Fe_{1-y}S$ (reactions 1 and 3, Fig. 3a, site (3), Fig. 3b, site (4)) and the sulphide surface centres (Fig. 3a, site (2), Fig. 3b, site (3)). At pH 10 or more the floatability of treated minerals is like the natural galena floatability due to surface nucleation of $Pb(OH)_2$ (Ralston and Healy, 1980).

It follows from the above considerations that in the presence of Pb(II) several types of surface lead-centres on galena (Fig. 6a, sites 2', 2", 3') and on sphalerite (Fig. 6b, sites 3', 3", 4') can be formed in an alkaline medium.

Adsorbed lead species at mineral surfaces interact with ethylxanthate ions, $(EX)^-$, as substantiated by the flotation test results (Fig. 1, curve 4 and Fig. 2, curve 4), electrokinetic measurements (Fig. 4, curves 3 and Fig. 5, curve 3), ATR–IR records (Fig. 7) and UV data.

The obtained ATR–IR data confirm very weak ethylxanthate ion adsorption on unactivated sphalerite in alkaline medium (Fig. 7a, spectrum 1), because Zn- and Fe-ethylxanthate are soluble compounds (Kakovsky, 1957), and EX^- adsorption on sites (1) and (2) (Fig. 6b) or ion-exchange reaction OH^- EX^- on site (5) or (6) are not thermodynamically favorable. However, Pb(II) causes a marked increase in the amount of surface adsorbed collector, so that characteristic bands of Pb-ethylxanthate are observed (Fig. 7a, spectra 2–4). With $3 \cdot 10^{-5}$mol dm^{-3} Pb(II), only the monolayer, chemically adsorbed –Pb–EX is formed (Fig. 7a, spectrum 2, 1198 cm^{-1}), for which

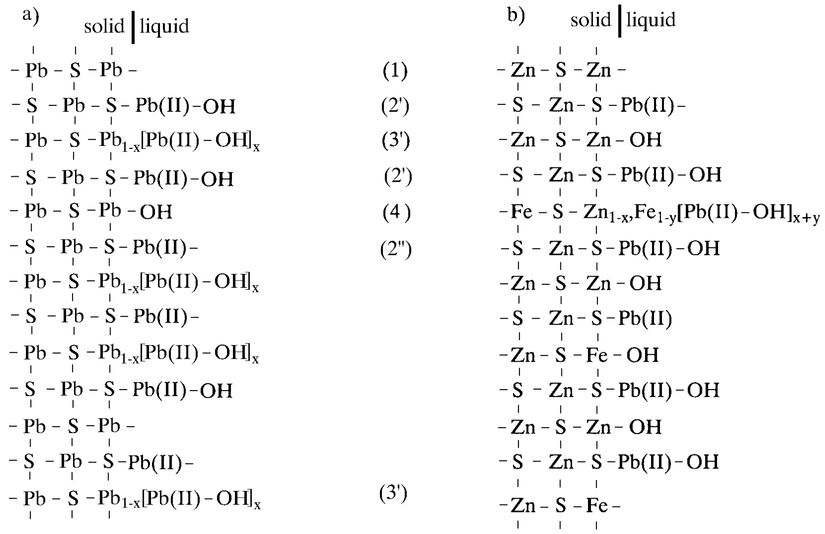

Fig. 6. Possible structure of the surface phase in the presence of dissolved Pb(II) in an alkaline medium of: (a) galena; (b) sphalerite

–C–O–C– stretching vibration below 1200 cm^{-1} is characteristic of a 1:1 coordination between the surface metal-ion (–Pb– from the mineral crystal lattice) and chemically adsorbed xanthate radical (Poling and Leja, 1963; Leja et al., 1963; Leppinen and Mielczarski, 1986; Mielczarski, 1986). The band intensity increased with the increasing lead ion concentration in the solution phase (Fig. 7a, spectra 3 and 4), providing an increase in the number of the surface lead sites for interaction with ethylxanthate. Also, the bands showed two maxima, 1190 and 1210 cm^{-1}, indicating the presence of monolayer, –Pb–EX (1190 cm^{-1}), and multilayer, physically adsorbed, stoichiometric $Pb(EX)_2$ (band above 1200 cm^{-1}) (Poling and Leja, 1963; Leja et al., 1963; Leppinen and Mielczarski, 1986; Mielczarski, 1986).

On galena untreated by lead, multilayer form of Pb-ethylxanthate is observed as the main adsorption product (Fig. 7b, spectrum 1). Pb-modified galena ethylxanthate band showed an increase in the monolayer $(EX)^-$ coverage of galena surface i.e. an amount of –Pb–EX (Fig. 7b, spectra 2–4, 1190 cm^{-1}) This result confirms the chemical adsorption of $Pb(OH)^+$ and Pb^{2+} and the increased number of lead sites for interaction with $(EX)^-$ ions.

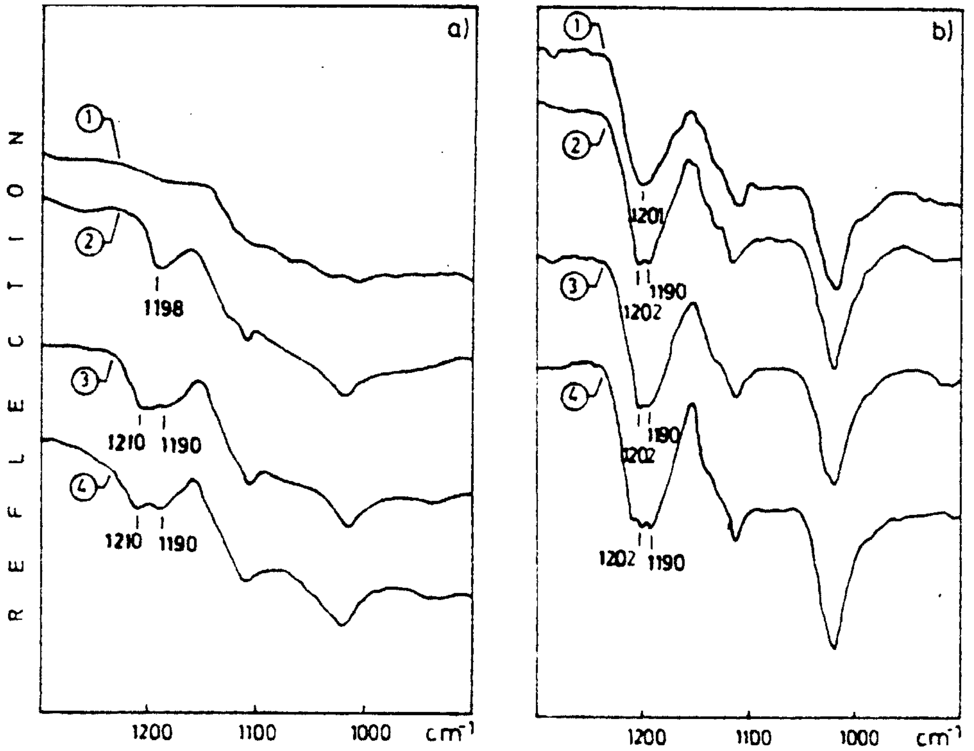

Fig. 7. IR reflection spectra of sphalerite (a) and galena (b) treated with: 1) KEX; 2) $3\cdot10^{-5}$ mol·dm^{-3} Pb(II), KEX; 3) $7\cdot10^{-5}$ mol·dm^{-3} Pb(II), KEX; 4) $1\cdot10^{-4}$ mol dm^{-3} Pb(II), KEX; (t_{Pb} = 15 min, t_{KEX} = 15 min, $c_{0KEX} = 3\cdot10^{-4}$ mol·dm^{-3}, pH = 8–9)

According to the obtained results, the surface reactions of mineral–Pb(II)–$(EX)^-$ interactions for alkaline media probably are:

1. Chemical adsorption of $Pb(OH)^+$ and in a lesser degree of Pb^{2+} ions and formation of M–Pb–OH and M–Pb– sites (M– galena or sphalerite), where Pb(II) is incorporated at the mineral lattice surface.

2. Surface nucleation of $Pb(OH)_2$ on the mineral, $M|Pb(OH)_2$; (| denotes surface).

3. a) Ion-exchange reaction between $(OH)^-$ from M–Pb–OH and $(EX)^-$.

$$M–Pb–OH + (EX)^- = M–Pb–EX + (OH)^- ;$$

b) Chemical adsorption of $(EX)^-$ on M–Pb– sites (zeta-potential M–Pb–EX is less positive or more negative than zeta-potential of Pb-modified minerals)

$$M–Pb– + (EX)^- = M–Pb–EX;$$

4. Ion-exchange reaction between $(OH)^-$ from $Pb(OH)_2$ and $(EX)^-$:

$$M \mid Pb(OH)_2 + 2(EX)^- = M \mid Pb(EX)_2 + 2(OH)^-;$$

or reaction between $PbOH^+$ (present in Outer Helmholtz plane of the Stern layer of electrical double layer) and EX^- ions

$$M \mid PbOH^+ + (EX)^- = M \mid PbOH(EX)$$

$$M \mid PbOH(EX) + (EX)^- = M \mid Pb(EX)_2$$

The dominant surface reaction strongly depends on the pulp pH and on the type of surface lead sites.

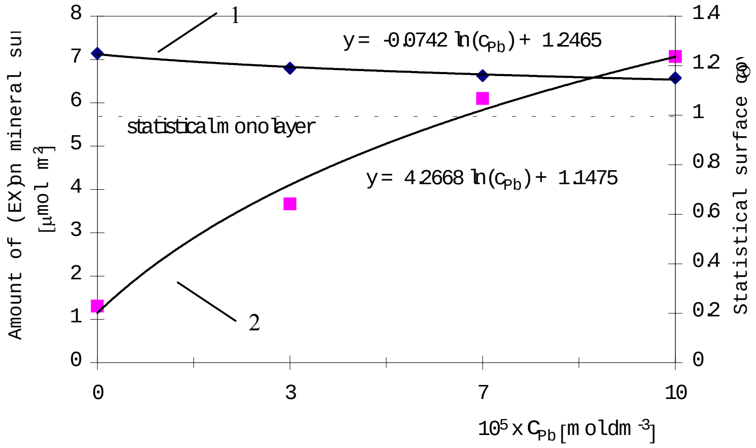

Fig. 8. Amount of $(EX)^-$, i.e. the statistical surface coverage of $(EX)^-$, θ, on galena (1) and sphalerite (2) as a function of Pb(II) concentration (t_{Pb} = 15 min, t_{KEX} = 15 min, $c_{0KEX} = 3\cdot10^{-4}$ mol·dm^{-3}, pH = 8–9)

The statistical ethylxanthate surface coverage on minerals, θ, was calculated using UV data. The value of Θ on Pb-modified galena decreases with the rise of Pb(II) solution concentration (Fig. 8, curve 1 $\Theta = -0.0742 \ln c_{Pb} + 1.2465$). The obtained result is in a good correlation with ATR–IR data according to the amount of monocoordinated $(EX)^-$ on Pb-treated galena increases with increasing of Pb(II) concentration (Fig. 7b, spectra 2–4). However, the statistical surface coverage of $(EX)^-$

on sphalerite increases when Pb(II) concentration increases up to $1\cdot10^{-4}$mol dm^{-3} Θ= 4.2668 lnc_{Pb} + 1.1475 (Fig. 8, curve 2).

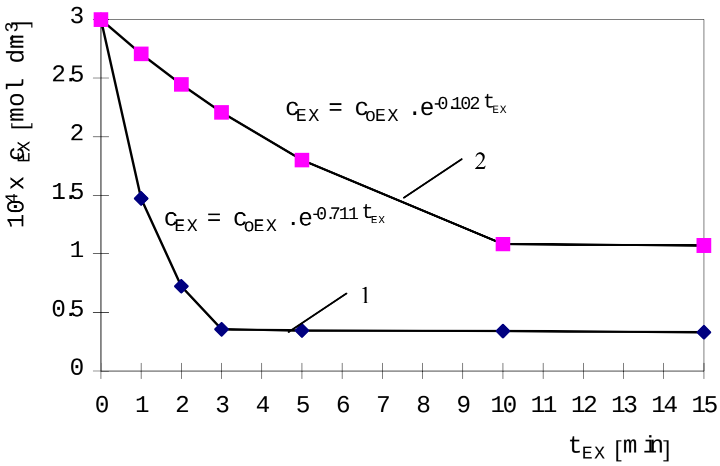

Fig. 9. Amount of $(EX)^-$, i.e. the statistical surface coverage of $(EX)^-$, θ, on galena (1) and sphalerite (2) in the function of KEX collection time; (t_{Pb} = 15 min, $c_{Pb} = 7\cdot10^{-5}$ mol·dm^{-3}, $c_{0\ KEX} = 3\cdot10^{-4}$ mol·dm^{-3}, pH = 8–9)

Kinetic studies showed that the interaction between Pb-modified galena and $(EX)^-$ ions is faster than between Pb-modified sphalerite and $(EX)^-$. For Pb-treated galena the KEX concentration in the solution decreases according to exponential equation of the collection time t, $c_{EX} = c_0e^{-0.711t}$ for t ≤ 3 minutes (Fig. 9, curve 1). The same type of curve was obtained for Pb-treated sphalerite, $c_{EX} = c_0e^{-0.102t}$, only for t (10 minutes (Fig. 9, curve 2). The dominant reaction (Pb-treated mineral–ethylxanthate ion) in flotation conditions is pseudo-first order, probably the ion-exchange reaction M–Pb–OH + $(EX)^-$ = M–Pb–EX +$(OH)^-$ (M – mineral), which contributes to the increase of the amount of chemically adsorbed, strongly bonded, monolayer –Pb–EX on the surface of either mineral, needed for good mineral flotatability. Near-equilibrium $(EX)^-$ adsorption on Pb-modified galena was obtained for 3 minutes, with the rate constant k = 0.711 min^{-1}, and for Pb-modified sphalerite for 10 minutes, with k = 0.102 min^{-1} (the solid phase activity is a = 1).

CONCLUSION

The obtained results showed that dissolved lead in an alkaline medium reduced natural galena floatability from pH 7 to 9.5, but activated sphalerite from pH 7.6 to

10.5. With K-ethylxanthate Pb-modified sphalerite floated nearly 100% through the alkaline pH range. Galena floatability was better only from pH 8 to 9.5 (85–95%).

The adsorption of lead cation species (Pb(OH)$^+$, Pb^{2+}) were confirmed by results of zeta-potential measurements. The identified surface products on Pb-modified minerals were –Pb–EX and Pb(EX)$_2$. On Pb-treated galena, the amount of –Pb–EX increases, i.e. the statistical surface coverage Θ of (EX)$^-$ decreases. Θ increases on Pb-modified sphalerite with the rising Pb(II) concentration in the solution. The dominant reaction between Pb-treated minerals and (EX)$^-$ on minerals is probably the ion-exchange reaction M–Pb–OH + (EX)$^-$ = M–Pb–EX +(OH)$^-$ of pseudo-first order. It is faster on Pb-modified galena surface (k = 0.711 min^{-1}, $t \leq 3$ minutes) than on Pb-modified sphalerite (k = 0.102 min^{-1}, t (10 minutes). The activation effect of lead on ethylxanthate adsorption on both minerals leads to the conclusion that recycled water which contains dissolved lead may be used in the process of selective galena/sphalerite flotation after galena has been floated, i.e. during the Zn-flotation.

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Badano wpływ jonów ołowiu (II) na powierzchniowe właściwości galeny i sfalerytu oraz kinetykę adsorpcji ksantogenianu etylowego w środowisku alkalicznym w celu określenia możliwości ponownego użycia wód flotacyjnych. Przeprowadzono flotacje i pomiary potencjału dzeta, które skorelowane z wynikami badań spektroskopowych w podczerwieni (ATR–IR) i ultrafiolecie (UV). Ołów zaadsorbowany na powierzchni galeny i sfalerytu jako $Pb(OH)^+$ oraz w mniejszym stopniu jako Pb^{+2}

redukuje flotowalność galeny w zakresie pH od 7 do 9,5 oraz ma silnie działanie aktywacyjne na naturalną flotowalność sfalerytu w zakresie pH od 7,6 do10,5. Na powierzchniach ziarn minerałów aktywowanych jonami ołowiu i wyflotowanych za pomocą ksantogenianu etylowo-potasowego wykryto obie formy ksantogenianu ołowiu tj. monowarstwę chemiczne zaadsorbowanego ksantogenianu (–Pb–EX) i wielowarstwę fizycznie zaadsorbowanego $(Pb(EX)_2$. Sfaleryt flotował prawie całkowicie w badanym zakresie pH, a galena flotowała lepiej tylko przy pH od 8 do 9,5 przy uzysku 85–95%. Główne reakcje zachodzące na powierzchni w zakresie pH 8–9,5 to prawdopodobnie reakcja wymiany M–Pb–OH + $(EX)^-$ = M–Pb–EX + $(OH)^-$, gdzie M oznacza minerał, co daje chemicznie zaadsorbowaną monowarstwę –Pb–EX na powierzchni minerału. Reakcja pomiędzy minerałem, który był modyfikowany jonami ołowiu i jonem $(EX)^-$ jest reakcją pseudo pierwszego rzędu. Na galenie modyfikowanej jonami ołowiu stała szybkości wynosi $k = 0{,}711\ \mathrm{min}^{-1}$ podczas gdy na modyfikowanym jonami ołowiu sfalerycie ma wartość $k = 0{,}102\ \mathrm{min}^{-1}$.