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CHEMICAL AND ELECTROCHEMICAL REACTIONS IN THE SYSTEM LEAD SULPHIDE – POTASSIUM ETHYL XANTHATE SOLUTION

Internal reflection spectroscopy (IRS) in the infra-red (IR) range of spectrum was used to follow the changes of the state of the lead sulphide surface during its oxidation and xanthate sorption. It was stated that the oxidation of the surface proceeds with the change in the surface stoichiometry (sulphur enrichment at the surface), but the reaction of xanthate sorption proceeds without significant changes in the surface stoichiometry. The results seem to corroborate the assumption that the sorption proceeds through the exchange of oxidation products or sulphide ions in the surface layer of sulphide by the xanthate ions from the solution without the oxidation of the surface during the sorption.

1. Introduction

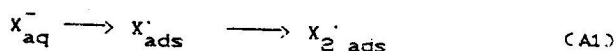
The adsorption of alkyl xanthates at the surface of lead sulphide has been studied since many years (Gaudin, 1963) and many different mechanisms were proposed for this process. Those mechanisms may be divided in three groups:

A) Electrochemical (mixed potential) mechanisms - the reaction of ethylxanthate sorption is an electrochemical oxidation reaction, with the reaction of the reduction of oxygen as a conjugate charge-balancing cathodic process (Woods, 1971, Ahmed, 1978, Pillai and Bockris, 1984). The reaction may proceed with the oxidation of the xanthate molecule giving the electrosorbed xanthate radical as the initial product of

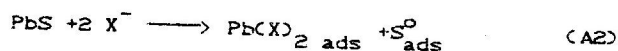
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reaction and the subsequent formation of dixanthogen as a final product (mechanism A1). In that case the PbS surface serves only as a mediator enabling the exchange of electrons. It may be schematically expressed as the following reaction:

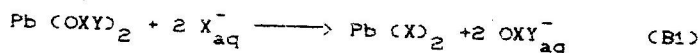


Otherwise sorption may proceed with the oxidation of the surface without the change of the oxidation state of xanthate molecule:

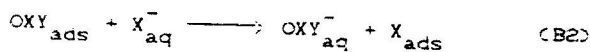


The difference between those two mechanisms is not only an academic problem - the oxidation of the surface with resulting formation of the sulphur or sulphur enriched nonstoichiometric sulphide (Buckley and Walker, 1988) may influence significantly the hydrophobicity of the surface.

B) Chemical (exchange with oxidation product) mechanisms - the sorption of xanthates proceeds as a reaction of xanthate ions from solution with the oxidation products of lead sulphide present at the surface as a consequence of previous oxidation by oxygen (Taggart, del Giudice and Ziehl 1934). The oxidation product may form the separate phase at the surface, when the surface is significantly oxidized, and the reaction may be written in that case as follow:

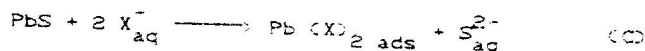


or the oxidation product may be present at the surface in low quantity (below one monolayer) and in that case reaction may be written:



where OXY means an anion of the oxidation product.

C) Exchange mechanism. According to that mechanism binding of xanthate to the surface proceeds via the exchange between the sulphide ions in the first layer and xanthate ions from solution:



The possibility that sorption proceeds according to that mechanism was considered in the early stage of development of flotation theory, (Gaudin, 1963), but was rejected off considerations in view of the very great difference in solubility products between PbS and lead xanthate. However Leppinen (Leppinen and Mielczarski, 1986) has showed that the reaction (C) does proceed when the lead sulphide is contacted with aqueous solution of xanthate. However the experiments of Leppinen have been performed in oxygen-free solutions, which automatically excludes the other mechanisms.

It was showed previously (Nowak, 1988) that the observation of free charge carriers absorption in the IR range of spectrum may give valuable information about the state of the surface of lead sulphide (especially the state of its oxidation). So, the IRS spectroscopy in the IR range of spectrum was used to follow the sorption of potassium ethyl xanthate from its aqueous air saturated solutions on the surface of lead sulphide, in the aim to differentiate between possible (listed above) mechanisms of xanthate sorption at the surface of PbS. Only the A2 mechanism assumes oxidation of the surface during sorption and both the B1 and B2 mechanisms assume the oxidation of the surface before the sorption.

2. Experimental

2. 1. Apparatus, reagents and experimental procedure

Lead sulphide in the form of thin (about 200 nm) layers was deposited on the surface of germanium reflection elements. More detailed description of the deposition procedure and the properties of such obtained layers may be found elsewhere (Nowak, 1988 and references cited therein). After having registered the spectrum of the freshly deposited layer the PbS sample was introduced to the solution of oxidizing reagent, the spectrum performed once again and the sample introduced to xanthate. After some time of sorption the sample was withdrawn from the solution and the spectrum of adsorbed product performed. Sometimes the spectra were taken several times in predetermined intervals of time during oxidation or sorption. Solutions were made using doubly distilled water and PA grade purity reagents, except potassium ethyl xanthate which was synthesized according to standard procedure and purified by crystallization. Experiments have been performed at room temperature and free access of air. Specord M 80 (Zeiss) spectrometer was used to record the spectra.

2. 2. Estimation of the magnitude of the free charge carriers absorption

The free charge carriers in semiconductor absorb IR radiation and the absorption coefficient may be expressed by the formula:

$$\alpha = N e^2 / m^* \tau \epsilon_0 \omega^2 = k N \lambda^2 \quad (1)$$

where α is the absorption coefficient, e - the charge of the electron, N - concentration of free charges, ω - frequency, λ - wavelength, m^* , ϵ_0 and τ constants characteristic for a given material and k - a proportionality constant. It may be readily showed, that for relatively low absorption the measured reflection coefficient may be expressed, for the case of IRS spectroscopy (Harrick, 1967), by the formula:

$$- \lg T = - \lg R^n = p n \alpha \quad (2)$$

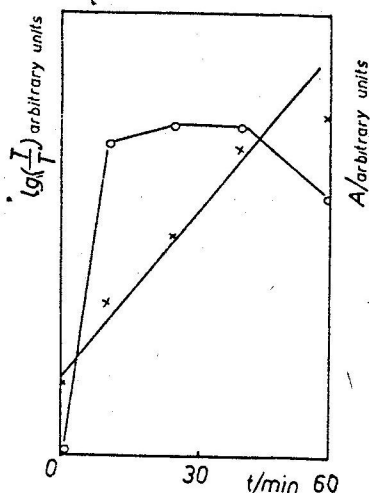
where n is the number of reflections in reflection element and p a proportionality constant. Combining the equations 1 and 2 one may readily show that comparing the transmittances of a sample at two different wavelength λ_1 and λ_2 one may estimate the concentration of free charge carriers with the accuracy to proportionality constant:

$$- \lg (T_1 / T_2) = p k n N (\lambda_1^2 - \lambda_2^2) \quad (3)$$

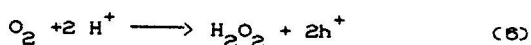
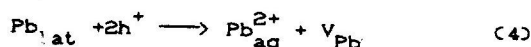
3. Results and discussion

Significant rise in the free charge carriers absorption was always observed during the oxidation of lead sulphide samples in aqueous solutions containing dissolved oxygen, which is presented in Fig. 1. The magnitude of that absorption was higher for acidic solutions and for the solution of H_2O_2 the free charge carriers absorption was so high that it masked any other features in the spectra. The products of surface oxidation were different, depending on the composition of solution. In the case of solutions in which lead salts are well soluble (ammonium acetate for example) the only observed oxidation products were the surface hydroxyl and carbonate groups. The free charge carriers absorption first rose quickly, next dropped to a constant value. The described behaviour is consistent with the following mechanism. During the oxidation lead ions go from the crystal lattice to the solution leaving lead vacancies in the surface layer of PbS. Those vacancies

Fig. 1 The changes of the free charge carriers absorption ($\text{---} \circ \text{---}$) and the absorptin band height of the oxidation product of the surface ($\text{---} \times \text{---}$) during the oxidation of the PbS surface in the 0.1 mol dm^{-3} ammonium acetate solution at the free access of air ($\lambda_1 = 975 \text{ cm}^{-1}$, $\lambda_2 = 1275 \text{ cm}^{-1}$). To follow the growing of the oxidation products at the surface 1530 cm^{-1} band was chosen which may be ascribed to surface carbonate or hydroxide groups.



undergo next the ionization according to equation:

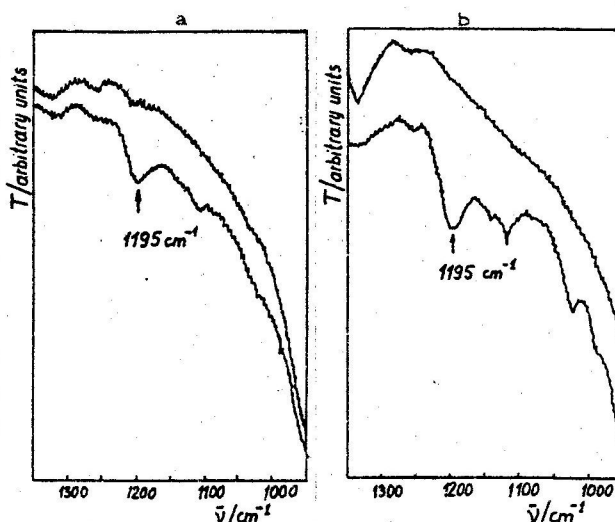


The holes consumed in reaction (4) are supplied in the reaction of reduction of dissolved oxygen - reaction (6) - however the large number of holes produced in reaction (5) rest at the surface, giving rise in enhanced concentration of holes at the surface and changing the properties of the surface to a p-type semiconductor, despite its initial character. After some time the concentration of lead vacancies at the surface becomes so high (much higher than the solubility of sulphur in the crystal lattice of PbS) that the elemental sulphur crystallize. At that moment the concentration of sulphur in the surface layer of PbS drops to equilibrium value. Note, that there is no formation of elemental sulphur in the initial period of oxidation. The elemental sulphur does not absorb IR radiation - the enhanced absorption in the IR region may only be ascribed to sulphur enrichment of the surface (according to reaction (4) which results in enhanced concentration of holes at the surface according to equation (5).

Fig. 2 The reflection spectra of two samples of lead sulphide before sorption (1) and after sorption in 10^{-2} mol dm $^{-3}$ KETX solution (2).

a - the sample kept before sorption in the 1 mol dm $^{-3}$ Na $_2$ S solution,

b - sample oxidized before sorption by oxygen dissolved in ammonium acetate solution.



There was no rise in the free charge carriers absorption during sorption but the quantity of the sorption product formed depended strongly on the degree of sample oxidation before sorption (measured as the free charge carriers absorption). The position of the most intense xanthate absorption band (about 1200 cm $^{-1}$) was characteristic for the adsorbed, strongly bound lead xanthate (Nowak, Mielczarski and Strojek, 1980), when the formation of multilayer coating with oxidation product was prevented. No formation of dixanthogen was ever observed. According to our estimation (Nowak, Mielczarski and Strojek, 1980) the quantity of the sorption product formed was always lower than one monolayer, providing that the sample was not too heavily oxidized.

4. Conclusions

The presented results show that the product of xanthate sorption on the surface of lead sulphide is formed according to mechanism (B2). However the mechanism (C) must not be excluded too. The extensive oxidation of the PbS surface introduces very large number of structural defects in the surface layer of PbS crystal. That changes the free energy of formation of PbS and may facilitate the sorption according to mechanism (C) too.

Acknowledgement

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5. References

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Streszczenie

Nowak, P., Chemiczne i elektrochemiczne reakcje w układzie siarczek ołowiu - etyloksantogenian potasowy, *Fizykochemiczne Problemy Mineralurgii*..21; 107-114.

Spektroskopia całkowitego wewnętrznego odbicia w zakresie promieniowania podczerwonego została użyta do badania zmian zachodzących na powierzchni siarczku ołowianego w czasie utleniania i sorpcji ksantogenianu. Stwierdzono, że w czasie utleniania powierzchni następuje

zmiana jej stechiometrii (wzbogacenie w siarkę), ale sama sorpcja przebiega bez zmian stechiometrii powierzchni. Rezultaty zdają się potwierdzać przypuszczenie, że sorpcja zachodzi na drodze wymiany pomiędzy jonem ksantogenianu, z roztworu a składnikami warstwy powierzchniowej siarczku, bez utleniania powierzchni w czasie sorpcji.

СОДЕРЖАНИЕ

П.Новак, 1989. Химические и электрохимические реакции в системе сульфид свинца - водный раствор ксантогената. Физикохимические вопросы обогащения, 21; 107-114.

Методом спектроскопии и полного внутреннего отражения ИКВВ в инфракрасной области спектра изучены превращения состояния поверхности сульфида свинца во время окисления и сорбции ксантогената. Обнаружено, что окисление поверхности происходит с повышением концентрации серы в поверхностном слое сульфида. Предлагается, что сорбция происходит за счет замены сульфидных ионов или ионов продуктов окисления ксантогенатными ионами.