

Optical luminescence studies of diffusion times at the potassium ethyl xanthate adsorption layer on the surface of sphalerite minerals

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Abstract. We propose reflectance measurements as a method for the evaluation of the kinetics of adsorption processes, to compute the diffusion times of the adsorption products at the thin layers formed at the sphalerite natural mineral-potassium ethyl xanthate solution interface. The method is based on the intensity measurement of the reflected monochromatic radiation obtained from the mineral-xanthate thin layer as a function of time. These determinations were made at the thin layer formed between the sphalerite or activated sphalerite natural minerals with potassium ethyl xanthate, for different solutions concentrations and pH values at constant temperature. Diffusion times of desorbed molecular species into the liquid bring important information about the global kinetics of the ions in this phase during adsorption processes at interfaces. Analysing the time dependence of this parameter one concluded on the diffusion properties of the xanthate molecule in the solution depending on its concentration and pH, knowing that at the initial time these molecules had a uniform spread. This method enabled us to determine that, in time interval of approximately 35 minutes to achieve dynamic equilibrium in the formation of the interface layer, one had three different kinetic behaviours of our systems. In the first 5-8 min one had highly adsorbent character, the state of equilibrium is followed by low adsorbent properties. Gaining information on the adsorption kinetics in the case of xanthate on mineral surface leads to the optimization of the industrial froth flotation process.

1. Introduction

Studying chemisorption and physical adsorption involves the description and characterization of the dynamical processes at the interface level. While liquids and solutions have homogenous properties, the position of atoms in solids is fixed, giving birth to inhomogeneous and complex structures at the boundary. This raises the special interest in the study of adsorption processes at solid-liquid interface from both theoretical and practical point of view.

Isotherm models that specify the requirements for a molecule to be adsorbed on the adsorbent surface were constructed. The description of such processes [1-5] and a study by best-fit numerical



methods determines the process parameters. But thermodynamic equilibrium is reached only at the end of the adsorption process, this is why specific kinetic modelling must be used to determine the parameters involved in the evolution of the interface layer. Kinetic adsorption models are also widely used [6-9]. These methods were applied in industrial [10-13] and environmental pollution reduction processes [14], [15].

A key feature of the kinetic determinations made in the case of dynamic phenomena like adsorption-desorption must take into account the characteristics of the two phases. The mathematical description must be linked to physical quantities describing the complex mechanisms that are present, such as diffusion in surface at liquid-solid interfaces, viscoelastic effects in the fluid phase, or exchange between bulk and the surface when the surfactants are soluble [16-18]. Diffusion mechanisms in the liquid phase can be described generally resorting to the Mandelbrot random walks [19] of the absorbed molecules on the adsorbent surfaces. One step in this fractal system, starting with desorption, followed by bulk diffusion and finished with a re-adsorption somewhere else, can be from a large Lévy jump up to a Lévy flight. The exponent of the power law distribution of the step size in a fixed period of time is between 1 and 3 [20]. It is known that only for power-laws with an exponent bigger or equal with 3 one can obtain the Gaussian distribution applying the central limit theorem. In the case of many adsorption-desorption processes this theorem cannot be used and one deals with Lévy distributions.

To be operational, the theoretical models discussed above need the experimental determination of the parameters directly linked to the internal mechanism of the phenomenon that is described. The experimental technique must permit continuous “in situ” determinations to be made, and it must not interfere with the delicate evolution of the physical and chemical processes at the adsorption interface. The repeatability of the determinations must be assured by choosing the same area from the solid state, especially when we talk about the adsorption on natural mineral surfaces.

Our determinations can lead to the elucidation of the kinetic models that can describe the adsorption-desorption processes at the interface between the sphalerite and activated sphalerite natural minerals and potassium ethyl xanthate solution, as well to the computation of some kinetic parameters at the interface level, or to the description of the diffusion of the sorbate molecules in the liquid. This work can be applied directly in optimization of the flotation process of this mineral.

2. Theoretical model, sample and experimental setup

2.1. Theoretical model

A complex theoretical model that can be applied in the description of the adsorption processes at the interface between the sphalerite or activated sphalerite natural minerals and potassium ethyl xanthate solution is widely described in the work of Bychuk and O'Shaughnessy [16-18], although in these articles only theoretical considerations and numerical simulations are made.

The problem is the correlation between the diffusion of the adsorbed molecule in the liquid solution, where it is found initially, and the adsorption-desorption rate of the flotation reagent. These three processes must be taken into account at the moment when the dynamic equilibrium is reached at the surface level. The adsorbed state of the flotation reagent is linked to the average speed of the molecules describing the drift of the particles. Capture domains or capture distances can be defined as the distances over which mass transport mechanism can act due to energetic and electrical modifications that take place at the solid-liquid interface due to adsorption.

The solid-liquid interfaces can be classified as a strong or weak system, depending on their kinetic properties. Strong systems are characterized by high attractive and retentive properties, contrary to the weak ones; depending on the ratio between the time of an adsorbed molecule to be desorbed Q^{-1} and the diffusion time t_h . Comparison of these two quantities permits an evaluation of the evolution trends at a microscopic level at the solid-liquid interface. Supposing that in a certain period of time the diffusion time t_h is small, resulting in many ions originating from the liquid phase reaching the surface of the solid. On the other hand, when desorption time Q^{-1} is small, one deals with many desorbed ions

from the solid surface. That is why their ratio gives a synthetic image of the global kinetic processes at the xanthate-mineral surface.

In the case of the weak systems the diffusion time is much smaller than desorption time one has:

$$Qt_h \ll 1 \quad (1)$$

while for the strong ones, diffusion is much stronger than desorption:

$$Qt_h \gg 1 \quad (2)$$

Taking into account the adsorption-desorption processes one can have the situation that is described in the followings. When the adsorption time is much smaller than desorption time it is very likely that a desorbed particle to be replaced by resorbed one in the adsorption process. These re-adsorbed particles can originate from a higher distance than the one that was desorbed, leading to the Lévy distribution of the steps in the random walk of the flotation reagent ions. Of course the particles that are adsorbed first are the ones from the immediate neighbourhood of the solid surface. At later moment a sink will form due to mass displacements in the adsorption-desorption processes. It is easy to understand that these sinks only form for strong systems where adsorption time is much smaller than desorption time. This demonstrates that we can also take into account the re-adsorption time t^* to characterize strong and weak systems, defining as follows [16-18]:

$$t^* = \frac{1}{Q^2 t_h} \quad (3)$$

When one has $t^* \ll t_h$ diffusion is much stronger than re-adsorption and one deals with volume diffusive characteristics, so that a strong system is characterized by:

$$Qt^* \ll 1 \quad (4)$$

A weak system has sufficient time to re-establish the equilibrium in the volume before re-adsorption happens $t^* \gg t_h$ leading to:

$$t^* Q \gg 1 \quad (5)$$

Denoting with $\Gamma(t)$ the equilibrium concentration of the adsorbed reagent at the solid surface at a certain moment in time and following the formulation from [16-18] one can deduce that the ratio $\Gamma(t)/\Gamma^{eq}$ is a function of $(t/t_h)^{1/2}$ where Γ^{eq} is the equilibrium concentration of the adsorbed reagent at the solid surface when the adsorption process ended and dynamic equilibrium was established.

2.2. Sample description and preparation

Sphalerite mineral samples were extracted from the Nistru mine, located in the mining basin of Maramures, Romania [21]. A single sample was selected for our determinations, with sufficiently large dimensions to be cut and polished. The cutting direction was arbitrary, not linked to the crystal structure of the mineral in question. The sample was chosen in such a way that it could contain, as long as it was possible, a single type of mineral with a relatively high structural homogeneity in his volume.

The inclusion of foreign chemical elements in our sample, other than the principal constituents of the sphalerite mineral, was checked using qualitative and semi-quantitative spectrographic measurements. For the microelements determined to be present in the sample we give their determined concentration: Sb (1000ppm), Sn (300ppm), Cd (100ppm), respectively Bi and Co (30ppm). The following chemical elements were below detection limit: As, Te, Hg, Ge, W, Mn, Ga, Cr, Ni, Mo, V, Ti, Tl, Be, In, Ag. We can say that the natural mineral that was used in our study has a close elemental composition to that of the pure crystal. But we must to take into that the natural minerals differs from

artificially grown single crystals due to energetic, structural and geometrical defects, because of surface roughness and punctual, directional, planar or other crystalline defects. Ignoring the differences between natural minerals and artificially grown single crystals can lead to experimental errors and misinterpretation of the experimental data.

Although the oxidation of mineral surfaces is a natural process and can be present during industrial flotation, the existence of the oxide layer introduces a second layer at the mineral-xanthate solution interface and new, unwanted variable in our study. To obtain a large experimental surface, clean at atomic level, a series of physical and chemical methods were applied due to the high contamination of our initial sample. To obtain a low surface roughness the sample surface was polished mechanically with abrasive glass down to 250µm level, abrasive powder to 10µm level and finally using Al₂O₃ with a granulation of 0.02µm, obtaining a levelled experimental surface with controlled roughness. To remove the oxide layer formed during polishing the chemical process of 3 consecutive washes for a period of 3 minutes in concentrated HNO₃ at room temperature was employed [22]. The chemical neutralization of the surface was achieved washing the surface with double distilled water. To remove the last gaseous atomic or molecular species, attached to the experimental surface the sample was introduced in a low pressure chamber (10⁻⁹Torr) where it was bombarded by a spray of argon atoms. Another current method of chemical surface cleaning, using H₂SO₄ with a pH of approximately 2 for 20-30 minutes, followed by 5-6 rinses in double distilled water, and finally a drying using hot air spray, was also tried, but stirring the sample lead to the destruction of the experimental plane surface.

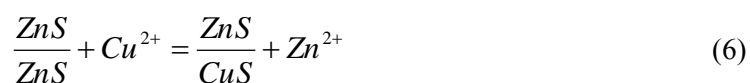
Potassium ethyl xanthate was used in our determinations because of faster crystallization times. It was obtained from an industrial grade one with a purity of 65%, diluted in acetone 4 times, followed each time by a precipitation in ethyl-ether, so a 99.9% pure xanthate was obtained. Knowing that xanthate molecules decompose in aqueous solutions, depending on the pH of the solution and the concentration of dissolved oxygen molecules, a quality check of the flotation reagent was made before each determination. This assessment was made using a Specord M-40 spectrophotometer in the UV domain of 200-400nm, knowing that the absorption characteristic of the xanthate molecule in aqueous solution is most pronounced here. The pH of the solution was fixed using analytical grade HCl and NaOH.

2.3. Experimental setup

The experimental method we propose for the in-situ determination of the kinetics for the adsorption process is reflectivity measurements of the interface layer. The determinations were made in an interval of 38-40 minutes during which the measured parameters reach a constant value.

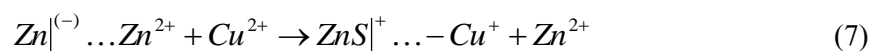
The concentrations of the potassium ethyl xanthate solution used were: 10mg/l, 25mg/l, 50mg/l, 100mg/l and 3000mg/l and for each concentration the following values for the pH: 7, 8, 9 and 10 were fixed. Using different values of the pH one could evaluate the influence of the decomposition of the xanthate with time on the adsorption process. The floatability is maximal in this interval. For pH values lower than 5 floating and adsorption is almost non-existent due to the rapid degradation of the xanthate in solution. For values higher than 10 any increase in this parameter produces very low variations in the process.

Knowing that natural sphalerite presents low adsorption properties, and that in industrial regime activation process is used before flotation, we also studied the adsorption of xanthate on the activated mineral surface. To increase the number of the oriented adsorption centres for the collector reagent at the surface a CuSO₄ solution of 310g/l was used for 30 minutes. The mechanism of the activation with copper sulphate, which facilitates the bond of the xanthogenate, is:



In this way more powerful anodic regions are formed, facilitating the attachment of the polar group of the collector reagent. Electron spin resonance (RES) determinations showed that the Cu²⁺ ion

interacts with the sphalerite mineral lattice ZnS by electron capture, integrating a monovalent Cu^+ ion in the lattice, based on the mechanism [23]:



This way the number of Cu^{2+} ions in the solution decrease and the number of Zn^{2+} ions increase by the same value [24].

The working temperature was fixed to the value most probable in industrial applications of 18°C using a thermostat [25].

The volume of the xanthate solution used in each determination was also fixed to 5ml to ensure a high rate of reproducibility for our measurements. Multiple determinations were also made for each experimental setup. After each determination the sample was cleaned using pickle liquor, and the fast drying process was aided by a spray of air. The planar experimental surface was positioned in a perfectly horizontal position using two parallel beams of laser radiation obtained from a He-Ne laser, and the aforementioned xanthate volume was placed on the surface.

In each set of determinations only one of the working parameters (mineral, concentration or pH) was modified while the others were kept constant.

The schematic representation of the experimental setup used in our reflectivity determinations can be seen in Figure 1.

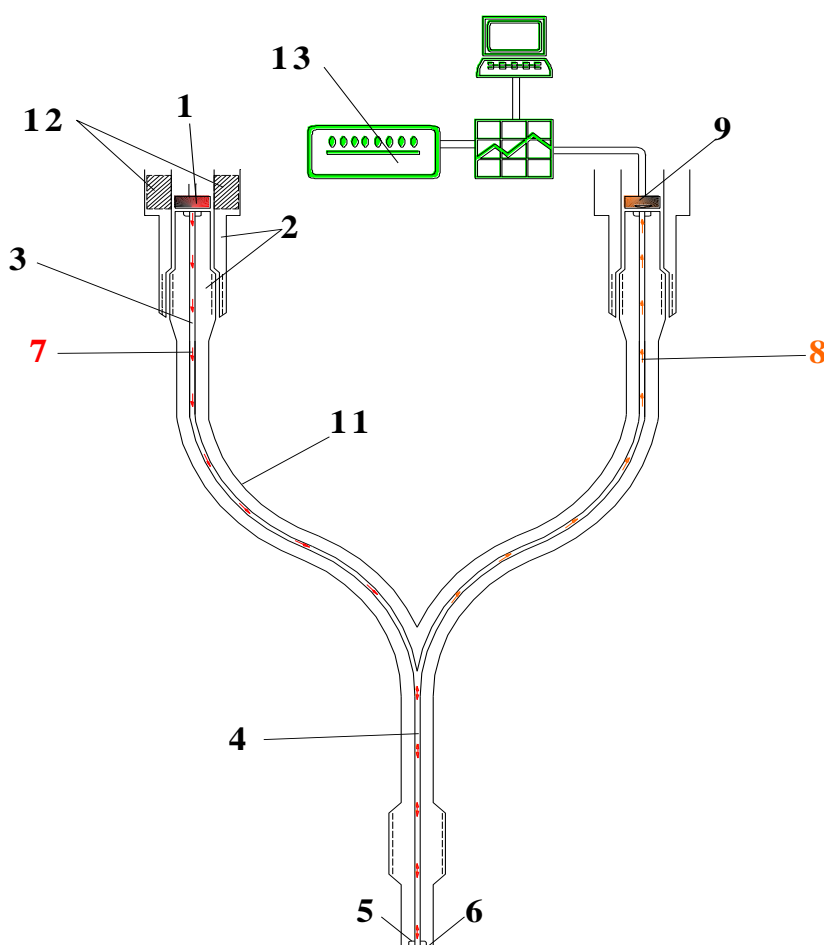


Figure 1. Schematic configuration of the experimental setup used for in-situ reflectometry measurements radiation in the case of the sphalerite mineral-ethyl xanthate solution interface. 1-GaAs laser source; 2-cooler; 3,7,8-transmission optical fibre; 4-the common channel for the optical radiation; 5,6-lenses; 9-photodetector; 10-recording system; 11-Teflon protection; 12-liquid nitrogen cooling system

Prior to proceed with the experimental reflectivity determinations one must specify the wavelength of the incident radiation. Its source must be stable and the radiation monochromatic. The wavelength

in use must be well transmitted in the xanthate solution and strongly reflected by the working surface. This wavelength must be sufficiently long so that the reflected signal will not be influenced by the structural defects found on the mineral surface. But IR and far IR radiations can contribute to the decomposition of the xanthate molecules and act as a catalyst, so this domain should be avoided as much as possible. The spectrophotometric measurements were made using the Specord M40 UV-VIS-NIR spectrophotometer. The transmittance of double distilled water and of the xanthate solutions that were used (above 90%) and the reflectance of the sphalerite mineral (above 75%) was found to be the highest in the 800-920nm domain, without entering deeper in the IR region. These values were determined using a calibrated aluminium mirror, which was used in all other determinations. This is why the wavelength of choice was that of a GaAs laser with $\lambda=0.89\mu\text{m}$. The problem of collimation was also solved using the laser.

After the determination of the temperature dependence of the laser radiation wavelength, the laser device was stabilised at a photon energy of 1.431eV using a liquid nitrogen cooling system, at a temperature of 253K.

Three Y shaped optical fibres were used consecutively to direct the laser radiation to the experimental surface, and to collect the reflected radiation. The fibres were constructed as common channel distributor, so that the region immersed in the xanthate solution acted both as the light source and the receptor for the reflected radiation [26]. The material used to construct the fibres was quartz, and the diameters were of 10 μm , 20 μm and 60 μm with a length of 1m. Noise reduction in the fibre was achieved by covering them with Teflon. Long focal distance quartz lenses were used at the emitter/receptor end of the optical fibre to parallelize the beam. The photodetector had a good sensibility in the chosen NIR domain. The distance between the mineral surface and the optical fibre was fixed to 3mm during all our determinations.

For the repeatability of the measurements one checked the time independence of the reflectance for the pure mineral surface and mineral-double distilled water interface, which remained constant in time.

3. Results and discussions

Using the experimental setup described above the reflected radiation from the solid-liquid interface was transformed to a voltage characteristic as in our other type of experimental determinations [21], [27]. Such way the evolution of the xanthate adsorption process on the mineral surface is described by the voltage-time graphs, linking the studied phenomenon through the modification of the intensity of reflected radiation to the time dependent voltage characteristics. We must point out that the voltage output of the photodetector is directly proportional with the intensity of the reflected radiation obtained from the optically stimulated surface that is why it is also proportional with the concentration molecules in the interface layer. The reflectance values were recorded continuously for a time interval of 38-40min.

As pointed out in the theoretical description of the adsorption process, the diffusion time of the sorbate molecules in the liquid phase t_h characterizes the global kinetics of the free radicals resulted from the xanthate molecule in the solution. Our “in situ” measurements permitted an uninterrupted monitoring of the adsorption process at the interface level. The adsorption-desorption dynamic equilibrium was reached in every determination in a time shorter than 35 min, so we can consider the reflectance value measured at this moment as a characteristic for I^{eq} . This value was used in all further computations. The characteristic graphs of the diffusion time as a function of time are presented in Figure 2 for activated sphalerite and 3 for non-activated sphalerite for the pH values of 7, 8, 9, 10 and xanthate solution concentration of 10mg/l, 25mg/l, 50mg/l, 100mg/l and 3000mg/l. It is well understood that in each determination only one parameter from mineral type, pH and solution concentration was changed.

One can observe that in every case the diffusion time has a fast decreasing speed in the first 5-6 minutes from the start of the adsorption process. A minimum is touched around this moment, and then a slow increase starts.

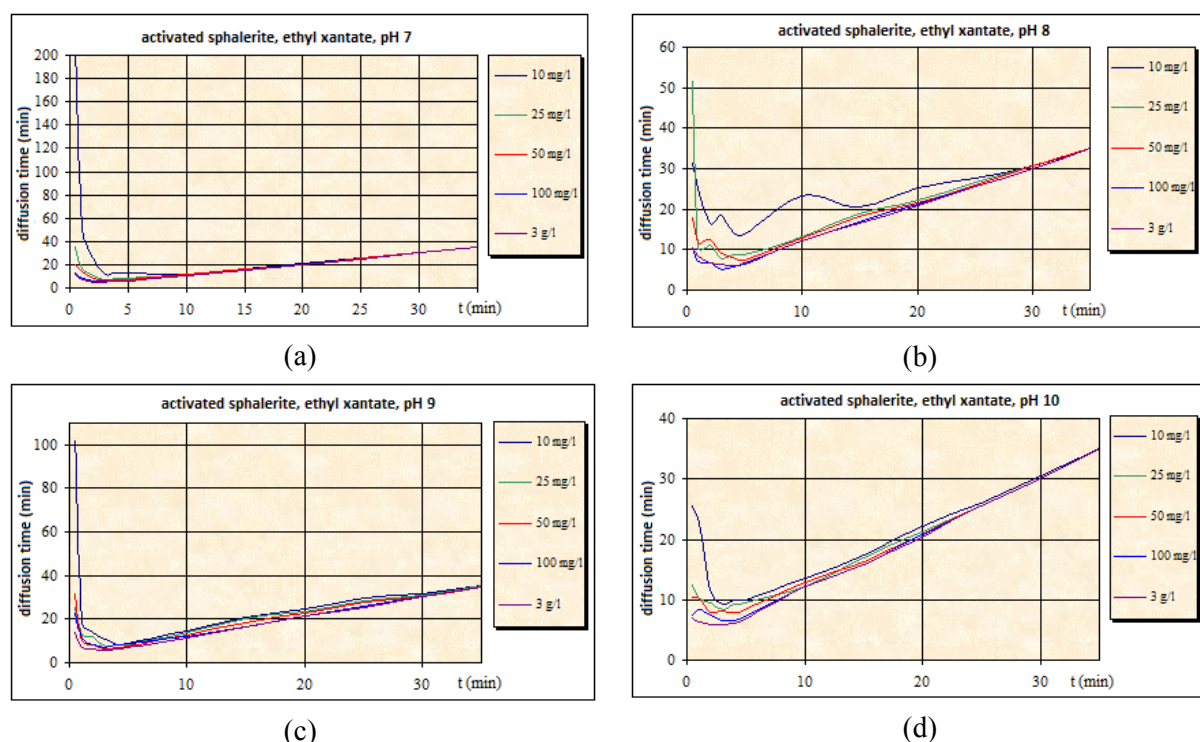


Figure 2. Diffusion times for the K-ethyl xanthate on the surface of the copper activated natural sphalerite mineral for the pH of (a) 7, (b) 8, (c) 9 and (d) 10. The legend of every graph displays the colour coding for the solution concentrations used

At the first moment the distribution of the xanthate molecules in the solution is uniform. The diffusion time at this moment represents the time to reach the interface layer for the molecules that are in the capture domain. One should resort to an explanation using the mass centre of the molecules in this domain. When the adsorption process starts the distance between the mass centre and the interface is maximal, and the average diffusion speed is zero. As the adsorption starts, the molecules that can be adsorbed are attracted to the surface of the solid, a net mass movement starts, the mass centre of the flotation reagent molecules gets ever closer to the interface layer, and the diffusion time to the interface drops significantly.

In the period of time around the moment when the diffusion time has its minimum, electrostatic forces appear at interface layer, blocking other xanthate molecules that are not close enough, to reach the interface. This way a second layer is formed. The accumulation of other molecular or ionic species at the solid-liquid interface is stopped, and a dynamic saturation is reached. Now we can say that the movement of mass centre towards the interface stops, and it slowly starts to move further away. This simplistic phenomenological explanation originates from the supposition that the capture domain is isolated from the rest of the solution.

One also can conclude that in the first 5-8 minutes after the adsorption process starts, all systems are strong ones, and after the period when $t \approx t_h$ a weak system is observed.

In the case of activated sphalerite, one can observe that at the pH levels of 8, 9 and 10 all graph present three maxima in the characteristic. This shows that the theoretical model that was used cannot fully describe the complex processes of chemisorption, physical adsorption, distribution of the adsorbent centres, lateral interactions between adsorbed species, etc., that take place at the interface level. Indirectly, these oscillations reflect the evolution of the energy distribution on the interface layer. Measurements of the electrical properties of this double electric film would be necessary to fully

elucidate the energy distribution. These measurements are not feasible because it would interfere with the complex and delicate mechanism of adsorption.

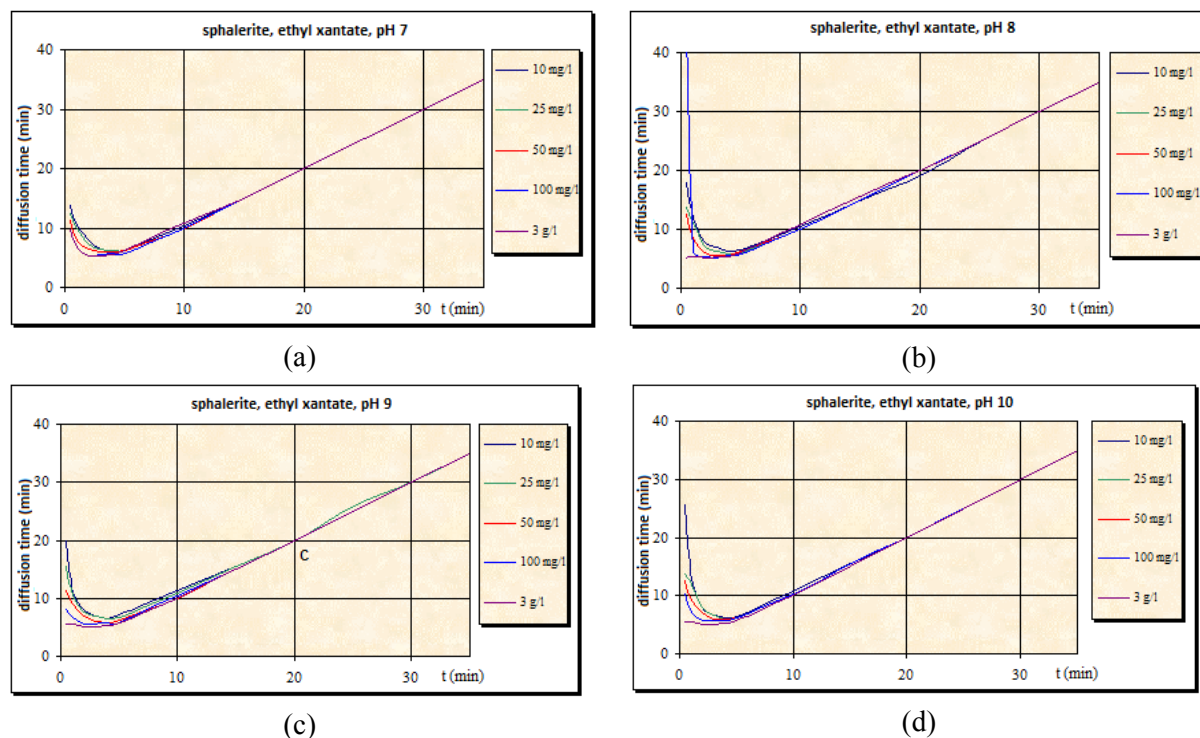


Figure 3. Diffusion times for the K-ethyl xanthate on the surface of the natural sphalerite mineral for the pH of (a) 7, (b) 8, (c) 9 and (d) 10. The legend of every graph displays the colour coding for the solution concentrations used

In the case of natural non-activated sphalerite the most important features are the very low values of the diffusion time at the start of the adsorption process. These are 8-10 times smaller than in the case of the activated mineral, demonstrating once again its low adsorption properties. The minima of t_h is located at a moment that is later by 2-3 minutes than in the activated case. One cannot observe the oscillations of the diffusion time in the tail. The values of t_h are greater at the end of the adsorption period than at the beginning of the process.

4. Conclusions

In this article we propose optical reflectivity studies as a method to determine the kinetic development of the sphalerite natural mineral – potassium ethyl xanthate interface layer. The quantity under investigation is the diffusion time of the flotation reagent in an aqueous solution, discriminating between systems with strong or weak adsorption properties. Studies on both non-activated and copper-activated sphalerites were conducted. Multiple pH values and solution concentrations were chosen to see their influence on the dynamic development of the interface layer. The mineral-xanthate interface develops as a strong system for the first 5-8 minutes, reaches a local minimum in the adsorption kinetics, after which it exhibits properties characteristic to weak systems. Diffusion time decreases with the increase of the concentration of the xanthate solution for the period of time when the system can be considered strong. It has its biggest overall values for a pH of the solution of around 8. The weak adsorbent properties of natural sphalerite are also reflected as 8-10 times smaller diffusion times compared to the Cu-activated sphalerite. Oscillatory behaviours of the diffusion time are displayed in all cases of the activated sphalerite-ethyl xanthate studies. These oscillations can be best observed for a pH of 8, indicating a more complex adsorption process than the one presented in the theoretical

considerations, requiring specialized determinations of electrical properties to study the energy distribution at the interface level.

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