Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 152 (2016) 591–595

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Optical luminescence studies of the ethyl xanthate adsorption layer on the surface of sphalerite minerals

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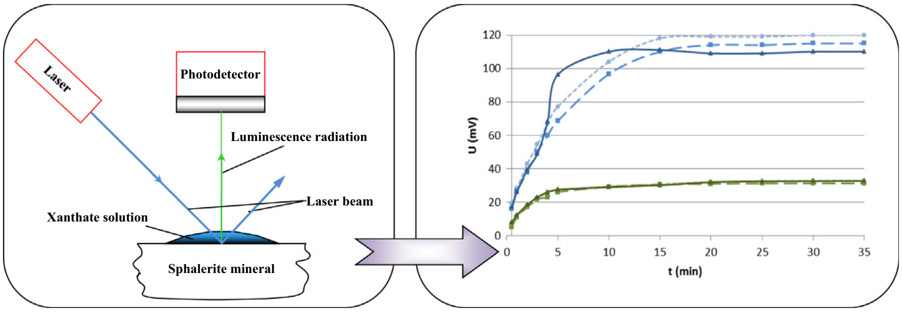
HIGHLIGHTS

- Measurement of luminescence radiation from sphalerite mineral–ethyl xanthate film.
- Time dependent determinations: different concentration, pH, at constant temperature.
- The kinetics of the adsorption process was determined.
- The time to achieve adsorption–desorption equilibrium was approximately 20 min.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 September 2014
Accepted 2 January 2015
Available online 13 January 2015

Keywords:
Sphalerite natural mineral
Potassium ethyl xanthate
Integral optical luminescence radiation
Interface layer dynamics
Adsorption–desorption equilibrium

ABSTRACT

In this work we propose optical luminescence measurements as a method to evaluate the kinetics of adsorption processes. Measurement of the intensity of the integral optical radiation obtained from the mineral–xanthate interface layer, stimulated with a monochromatic pulsating optical signal, as a function of time were made. The luminescence radiation was obtained from the thin interface layer formed at the separation surface between the sphalerite natural mineral and potassium ethyl xanthate solution, for different solution concentrations and pH-es at the constant industry standard temperature. This method enabled us to determine the time to achieve dynamic equilibrium in the formation of the interface layer of approximately 20 min, gaining information on the adsorption kinetics in the case of xanthate on mineral surface and leading to the optimization of the industrial froth flotation process.

Introduction

Chemical and physical adsorption processes have applications in industrial and technological processes, such as mineral flotation, modifying the flotation properties of the useful metallic compounds, and so, separating them from the gangue. In this case thin interface layers are formed between the collector reagent solutions, characterized by homogeneous properties in all their volume, and the solid phase, which have complex and inhomogeneous surface properties due to the fixed atomic positions. In the study of adsorption mechanisms one must take into account the dynamic modifications occurring mainly at the at the solid–liquid interface [1–3].

The key to understand the kinetic mechanisms in flotation processes is to study those that take place at the solid–liquid interface level and heave a great importance in the characterization of the interface phenomena. Mathematical and theoretical models were proposed with different levels of generalization. For example the adsorption–desorption phenomena can be coupled with the diffusion process in the liquid phase and experimental particularizations to specific solid–liquid interfaces were given [4,5]. From

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http://dx.doi.org/10.1016/j.saa.2015.01.001
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other point of view the isothermal equations can be established based on different models but just in the case of thermodynamic equilibrium. These statistical methods were not applied to in situ evaluations [5,6].

Xanthate molecules can be used to modify the floatability of many non-ferrous sulfurous minerals during flotation, so the dynamic in situ monitoring of such adsorption processes is an important step in the optimization of the industrial workflow [7–9].

We present integral optical luminescence measurements as a method to monitor the in situ kinetics of adsorption–desorption process. This way one can determine the onset of the dynamic equilibrium between the two phenomena at the interface layer formed between sphalerite natural mineral and potassium ethyl-xanthate solution, so the maximum amount of metallic mineral can be separated and no xanthate decomposition start to appear.

Samples and method

Sample description and preparation

Sphalerite mineral samples were extracted in the Nistru mine, located in the mining basin of Maramures, Romania. In this region the nonferrous mineral extraction and processing industry has an important role in the local and national economy. For our determinations a single sample was selected, 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 in our sample of foreign chemical elements, other than the principal constituents of the sphalerite mineral, was checked using qualitative and semi-quantitative spectrographic measurements. We give here the concentration of the microelements determined to be present in the sample: Sb (1000 ppm), Sn (300 ppm), Cd (100 ppm), respectively Bi and Co (30 ppm). 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 affirm that these elements are missing from our sample because their vast majority is not characteristic for the mine where the sample came from, or our mining region. Also 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 or crystalline defects. Ignoring the differences between natural minerals and artificially grown single crystals can lead to experimental errors and to the 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 this surface layer introduces a second layer at the mineral–xanthate solution interface, and a 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 250 μm level, abrasive powder to 10 μm level and finally using Al_2O_3 with a granulation of 0.02 μm, obtaining a flat 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 min in concentrated HNO_3 at room temperature was employed [10]. The chemical neutralization of the surface was made 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^{-9} torr) and bombarded by a jet of Ar atoms. This process ensures that the oxide layer does not form again for enough time for the measurements to be done correctly. We also tried another current method of chemical surface cleaning: the use of H_2SO_4 with a pH of approximately 2 for 20–30 min, followed by 5–6 rinses in double distilled water, and finally a drying it using hot air. In this case the stirring of the sample lead to the destruction of the experimental flat surface.

In our determinations we used potassium ethyl xanthate, because of faster crystallization times. It was obtained from a 65% pure (industrial grade) one, diluted in acetone 4 times, followed each time by a precipitation in ethyl-ether, so a 98.4% pure xanthate was obtained. Knowing that xanthate molecules decompose in aqueous solutions, depending on the pH of the solution and the oxygen molecules dissolved in the water, a quality check was made before each determination. This assessment was made using a Specord M-40 spectrophotometer in the UV domain of 200–400 nm, where the xanthate molecule in aqueous solution has its most pronounced absorption characteristic. The pH of the solution was fixed using analytical grade HCl and NaOH.

Experimental method

The experimental method we propose for the in situ determination of the adsorption process kinetics is optical luminescence measurements based on the determination of the integral optical radiation obtained from the adsorption layer stimulated by a pulsing monochromatic signal. The determinations were made during a time interval of 35 min after which the measured dynamic parameter became a constant. The time distribution of the measurements was as it follows: at 0.5 s after contact, every second in the domain 1–5 s, and every 5th second in the domain 5–35 s.

The concentrations of the potassium ethyl xanthate solution used were: 50 mg/l, 100 mg/l and 3000 mg/l. For each concentration the values of the pH of 7, 9 and 10 were prepared. 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 parameter 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 of 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. A $CuSO_4$ solution of 310 g/l for 30 min was used to increase the number of the oriented adsorption centers for the collector reagent at the surface. The activation mechanism with copper sulfate, which facilitates the bond of the xanthogenate, is:

$$\frac{\mathrm{ZnS}}{\mathrm{ZnS}} + \mathrm{Cu}^{2+} = \frac{\mathrm{ZnS}}{\mathrm{CuS}} + \mathrm{Zn}^{2+} \tag{1}$$

More powerful anodic regions are formed this way, facilitating the attachment of the polar group of the collector reagent. Electron spin resonance (RES) determinations showed that the bivalent Cu^{2+} ion interacts with the sphalerite mineral lattice ZnS by electron capture, integrating a monovalent Cu^{+} ion in the lattice, based on the mechanism [11]:

$$\mathrm{Zn}|^{(-)} \ldots \mathrm{Zn}^{2+} + \mathrm{Cu}^{2+} \rightarrow \mathrm{ZnS}|^{+} \ldots - \mathrm{Cu}^{+} + \mathrm{Zn}^{2+} \tag{2}$$