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Article

# Electrochemical Depression of Galena Aiming at Selective Sulfide Flotation

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Neste artigo, o potencial no qual a depressão da galena ocorre, é relacionado com a formação de compostos hidrofílicos em sua superfície. São propostas reações com base em voltametria cíclica, dados termodinâmicos e análises por espectroscopia de fotoelétrons. Variáveis eletroquímicas, tais como o potencial de oxirredução, apresentam boas perspectivas para a flotação seletiva da galena e esfalerita, pois numa dada faixa de potencial, a superfície da galena, ao contrário da esfalerita, se torna hidrofílica, conforme mostraram as medidas de ângulo de contato e testes de microflotação.

In this article, the potential at which galena depression occurs is related to the formation of hydrophilic compounds on its surface. Reactions are proposed based on analyses by cyclic voltammetry, thermodynamic data, and X-ray photoelectron spectroscopy (XPS). Electrochemical variables, such as the redox potential, present good perspectives for selectivity in the flotation of galena and sphalerite, because in a given range of potentials, the galena surface becomes hydrophilic, as shown by measurements of the contact angle and floatability tests.

**Keywords:** *galena electrochemistry, contact angle, depression, sphalerite*

## Introduction

The flotation of sulfide minerals, using ore with complex composition, has been extensively studied, as shown by literature reviews; the purpose is to obtain selectivity in the process[1-4]. Some depressants and activators are already well known, such as cyanide and zinc sulfate. In cases of mixtures of lead, copper, and zinc minerals , the selectivity is poor, and the lead concentrates become highly contaminated by the other minerals which originate from the lead ore.

The main lead ore is lead sulfide, galena, with a theoretical content of 86 wt% Pb. It occurs naturally, accompanied by other sulfides and gangue minerals. The classic process of ore dressing applies thiocollectors, such as xanthates, in a pH range of 8 to 9; the resulting concentrate is 60% Pb[5,6]. However, the mechanism of the reaction has not yet been solved[7,8]. The oldest theory[9] explains the process as one of adsorption, with ion exchange between the anions xanthate and sulfide occurring on the surface of the mineral. It is widely recognized that oxygen is essential to the flotation process[10-14].

In the first step of the chemical mechanism, the galena surface sulfide ion is oxidized, producing lead sulfate and thiosulfate, and the latter reacts with xanthate ion $X^-$, as follows[15]:

$$PbSO_{4(s)} + X^- \rightleftharpoons PbX_2 + SO_4^{2-} \qquad (1)$$

$$PbS_2O_3 + 2X^- \rightleftharpoons PbX_2 + S_2O_3^{2-} \qquad (2)$$

The hydrophobic character of the galena surface is attributed to $PbX_2$.

In the electrochemical mechanism, electrode reactions occur on the galena surface which is in contact with the aqueous solution containing xanthate ion, as follows[15]:

(a) anodic reaction of oxidation of the collector, giving rise to lead xanthate plus dithiolate:

$$PbS + 2X^- \rightleftharpoons PbX_2 + S0_2e^-PbS + 2X^- \rightleftharpoons PbX_2 + S^0 + 2e^- \quad (3)$$

$$2X^- \rightleftharpoons X_{2(s)} + 2e^- \quad (4)$$

(b) cathodic reaction of oxygen reduction, giving rise to hydroxyl ion:

$$1/2\ O_2 + H_2O \rightleftharpoons 2OH^- \quad (5)$$

Here, electrochemical techniques, such as cyclic voltammetry, are applied to establish the potentials corresponding to the significant reactions, and based on the results of chemical analysis, the products are identified. The hydrophilic character of these compounds is checked by contact angle measurements of polarized specimens and the galena depression effectiveness is confirmed by floatability tests carried out in a Hallimond tube. The objective of this study is strictly the verification of the applicability of the electrochemical depression of galena as a flotation technique in order to separate it from sphalerite.

## Experimental

The sample used was natural compact galena from the region of Boquira, in the state of Bahía, Brazil. By chemical analysis, the ore grade was 85.4% Pb and contaminant elements were 0,33% Zn, 0.28% Sb, and in decreasing order from 600 to 6 ppm, Cd, Fe, Ag, As, Bi, Cu, Mn, Cr, Mo, and Co.

The experimental work was carried out in three different steps:

(a) cyclic voltammetry, to recognize the potentials where significant reactions occurred, using an EG&G Princeton Applied Research Model 273A potentiostat and a Houston X-Y recorder,

(b) contact angles, determined with a Raméhart Mod. 100-00 goniometer,

(c) microflotation tests of electrochemically modified galena with a Hallimond tube, and finally, microflotation of natural sphalerite at several pHs.

In all steps, a 0.1 M KCl aqueous solution was used, with 3.7 x $10^{-4}$ M potassium ethyl xanthate; the pH was adjusted with KOH and KCl diluted solutions.

A classic electrochemical cell was used. The working electrode, with a 0.96 cm$^2$ area, was made by introducing a natural compact galena fragment into Teflon tube. The counter electrode was a platinum spiral, and the reference electrode was a saturated calomel electrode. A detailed description of the experimental apparatus is described elsewhere[16].

All electrochemical tests were conducted at ambient temperature (25 °C), and the pH was adjusted to 8.0, 9.0, 10.0, and 11.0; cyclic voltammetry scan rates were 4, 10, 20, 30, 40, and 60 mV/s. Prior to each test, a gas stream of pure nitrogen was bubbled through the solution for 30 min. The precision of the measurements was tested by replicate experiments.

The hydrophilic/hydrophobic character of the reaction products on the surface of the galena electrode was tested by measurement of the contact angles for polarized electrodes at different applied potentials selected from the voltammograms. For such a measurement, a Raméhart goniometer, Model 100-00, was used in conjunction with the electrochemical cell.

Microflotation with a Hallimond tube was carried out with previously electrochemically treated comminuted galena with a particle size of 208 μm, in an electrochemical cell, with a working electrode of particulate galena in a platinum basket. The particles were subject to several applied potentials, selected from previous tests, for 30 min each.

All of the potentials were referred to the IUPAC international convention, and referred to the sign convention hydrogen electrode, assuming the saturated calomel electrode has a potential of 0.245 V *vs.* S.H.E.

XPS measurement were carried out with a Perkin-Elmer 1257 spectrometer, using a Mg Kα X-ray source operated at 1253.6 eV. A pass energy of 46.85 eV was used for all elemental spectral regions. The counting time was 100 ms/step, corresponding to 0.1 eV/step. After the polarization tests the specimens were stored in a desiccator and then transferred to the XPS system, and their generated spectra are shown elsewhere[16].

## Results and Discussion

Reactions are proposed to justify the appearance of anodic and cathodic peaks on the cyclic voltammogram in Fig. 1. The reaction products were confirmed by XPS analysis, based on the estimated Pb:C ratio, after the application of the X-ray beam onto previously polarized samples by the utilization of selected potentials.

Studies carried out by Richardson and O'Dell[17] demonstrated that a galena surface is an n-type semiconductor, thus being sulfur deficient for potentials around -600 mV, so that the xanthate does not adsorb spontaneously onto

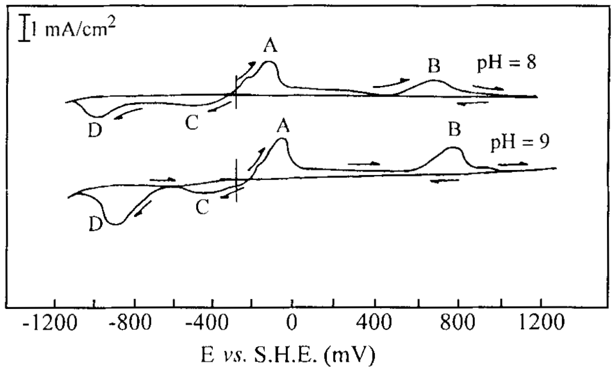
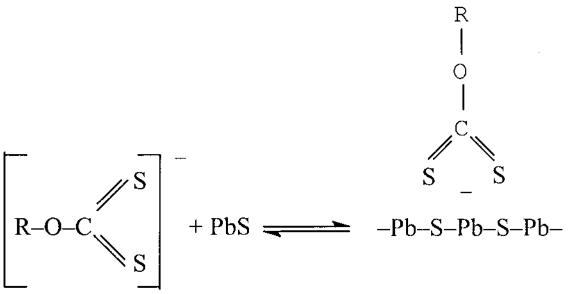


**Figure 1.** Typical cyclic voltammogram, obtained with an electrode of galena in an aqueous solution of KCl 0.1 M and 3.37 x $10^{-4}$ M potassium ethyl xanthate, at pH 8.0 and 9.0, with starting potential -280 mV (rest potential) and initial scan in the anodic direction. Sweep rate 10 mV/s.

galena surfaces. This was confirmed in the present study by XPS analysis of fresh galena samples which showed a Pb:S ratio of 1:0.61. On applying anodic potentials, the mineral exhibits p-type semiconductivity on its surface, and then xanthate is adsorbed spontaneously, as can be seen in Fig. 2 where the interval -600 to 200 mV corresponds to contact angle zero, that is, no xanthate adsorption. For potentials higher than 200mV, ethyl xanthate adsorbs spontaneously, characterized by contact angles around 30° [17].

At first, by pure chemical reaction, lead xanthate is formed on the mineral surface by a reaction of surface lead with the resonance hybrid, which leads to the complex with Pb[18]:



(6)

Under this condition, with sulfur in excess of lead, the surface becomes hydrophobic, which favors flotation.

With the application of an anodic potential, a pre-wave appears before peak A (Fig. 1), due to the electrochemical reaction (7), followed by two chemical steps, (8a) and (8b):

$$C_2H_5OCS_2^- \rightleftharpoons C_2H_5OCS_2 + 1e^- \quad (7)$$

$$C_2H_5OCS_2 \rightleftharpoons (C_2H_5OCS_2)_{ads} \quad (8a)$$

$$2(C_2H_5OCS_2)_{ads} \rightleftharpoons (C_2H_5OCS_2)_2 \quad (8b)$$

or, according to the overall reaction proposed by Woods[19]:

$$2(C_2H_5OCS_2)_{ads} + C_2H_5OCS_2^- \rightleftharpoons (C_2H_5OCS_2)_2 + 1e^- \quad (9)$$

This dixanthogen may react with the galena surface producing $Pb(C_2H_5OCS_2)_2$ [20]. As a matter of fact, when anodic scanning proceeds, peak A (Fig. 1) appears, which may be explained by the reaction:

$$PbS + C_2H_5OCS_2^- \rightleftharpoons Pb(C_2H_5OCS_2)_2 + S + 2e^- \quad (10)$$

in accordance with the $E_h$ *vs.* pH diagram for the galena-xanthate-water system[1] at pH 9. The presence of lead xanthate was corroborated by the ratio 8:1 of C:Pb in the XPS analysis, for a sample conditioned at -45 mV. At more positive potentials, the galena surface becomes hydrophobic, enhancing galena flotation, as shown in Figure 3a.

As anodic scanning proceeds, peak B (Fig. 1) appears at 800 mV, corresponding to the reaction:

$$Pb(C_2H_5OCS_2)_2 + 2H_2O \rightleftharpoons Pb(C_2H_5OCS_2)_2 + Pb(OH)_2 + 2H^+ + 2e^- \quad (11)$$

the products of which appear in the $E_h$ *vs.* pH diagram constructed by Woods[1]. The XPS analysis produced a higher C:Pb ratio, 14:1, as well as an increase in the oxygen content on the mineral surface. The hydrophobic character suggested that $X_2$ had been adsorbed on that surface.

From the inequality of the areas of peaks A and B it may be inferred that only part of the $PbX_2$ generated in reaction (10) is oxidized according to reaction (11). This may explain peak C (Fig. 1) according to reaction (12)

$$Pb(C_2H_5OCS_2)_2 + S + 2e- \rightleftharpoons PbS + C_2H_5OCS_2^- \quad (12)$$

as the reverse of reaction (10), starting at -225 mV. A sample collected at -478 mV showed a drop in the ratio for C:Pb to 2.8:1, as the xanthate removed from the surface entered the solution and the ratio Pb:S became *ca* 1.

Under the present conditions, the surface of galena should be free from the collector, and therefore, hydrophilic, as corroborated by measurements of the contact angle shown in Fig. 2; it may be observed that in this potential range (-650 to 50 mV) these angles were zero. Correspondingly, under these same conditions the floatability decayed dramatically to 10%, as may be observed in Fig. 3a. Another reaction that should be considered for peak C (Fig 1) is the hydrogen evolution, due to the reaction $2H + 2e^- = H_2$, which starts at -265 mV, for pH‘9.

Peak D (Fig. 1) has been generally attributed to dissolved oxygen reduction[20], but since in the present case the electrolyte was deaerated, this hypothesis becomes improbable. A possible explanation for this peak may be the partial decomposition of galena to metallic lead and hydrosulfide ion, at -574 mV *vs.* S.H.E. XPS analysis indicated a high carbon content on the galena surface, indicating the presence of some xanthate, which renders the mineral hydrophobic.

With an increase in the pH, anodic peaks were slightly displaced to more positive potentials, and changes in the

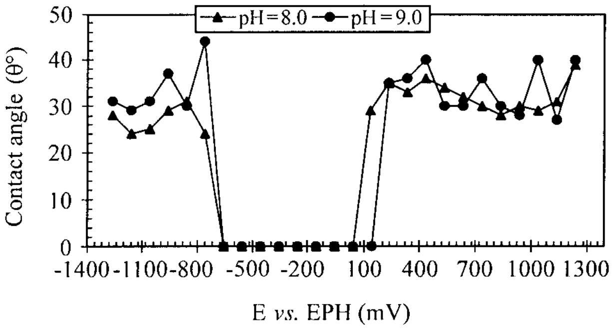


**Figure 2.** Contact angle measurements for galena at pH 8 and 9 under applied potentials from -1258 to 1242 mV, in an aqueous solution of KCl and 3.37 x $10^{-4}$ M potassium ethyl xanthate.

scanning rate did not cause remarkable differences, except in the peak heights.

In Fig. 2, which corresponds to pH 8 and 9, it is evident that in the range of -650 to +50 mV, the galena particle exhibited hydrophilic behavior, and the value of the contact angle decayed to 0°, implying that flotation of this mineral becomes thermodynamically impractical under the prevailing conditions.

The results from Fig. 2 may be confirmed by the profile observed in Fig. 3a where the floatability is related to the hydrophilic behavior, which prevents the adherence of bubbles to the mineral surface, and floatability decayed to 10% in the potential range of -500 to +100 mV.

Figure 3b shows the floatability behavior of sphalerite as a function of pH. It can be seen that sphalerite exhibits high floatability at pH 9, confirming the possibility of selective flotation of galena and sphalerite, as the latter does not respond to applied potentials, due to its high resistivity.

## Conclusions

Electrochemical techniques may be useful for the control of selective floatability of galena in the presence of sphalerite, a common association in complex natural ores.

The presence of hydrophilic surface compounds on galena may be recognized through contact angle measurements and floatability tests.

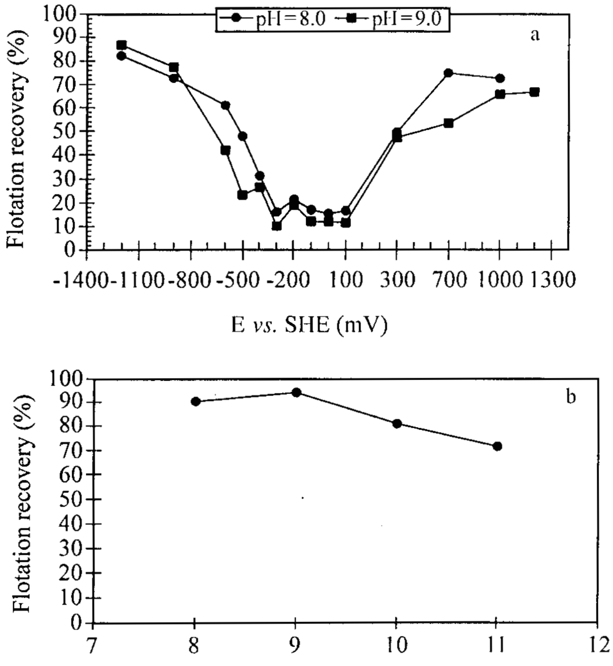


**Figure 3.** a: Influence of applied potentials on galena floatability in an aqueous solution of KCl and 3.37 x $10^{-4}$ M potassium ethyl xanthate. b: Influence of pH on the floatability of sphalerite in the same solution.

The application of adequate potentials to galena, under appropriate pH conditions in the presence of the collector potassium ethyl xanthate, causes surface reactions, generating hydrophilic compounds which depress galena, while sphalerite tends to float.

The electrochemical treatment depresses galena and not sphalerite (ZnS), an electrical insulator with an energy gap of $e_g$ = 3.7 eV[21], making it unresponsive to applied potentials, in contrast to galena and other semiconductor or quasi-metallic sulfides, which are reactive.

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