Cyclic voltammetry and dielectric studies on PbS–potassium ethyl xanthate–dextrine system under flotation and depression conditions

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Abstract

Froth flotation technique continues to be one of the most important concentration processes to float ores in a selective form specifically for PbS–ZnS, PbS–CuFeS₂ and PbS–ZnS, PbS–CuFeS₂ ores. There is an interest in doing research on a clean reagent (biodegradable reagent) to depress lead sulfide ore to control this process and have the appropriate knowledge about the interactions that can occur among galena and dextrine reagent. Cyclic voltammetry, high impedance and flotation test results are compared on a PbS–KEX–C₆H₈O₅ (galena–ethyl xanthate–dextrine) system to obtain the responsible collector and depression products and the suitable conditions to float and depress galena ores. Cyclic voltammetry studies showed the reaction products responsible for the shrink galena ore, in this case the PbC₆H₈O₅ organometallic. Measurements of complex permittivity and dielectric constant, at 100 MHz, by high impedance technique suggested that it is possible to obtain from isotherm adsorption the adequate industrial depressor this being in the range of 20–30 ppm.

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Keywords: Flotation; Galena; Ethyl xanthate; Dextrine; Cyclic voltammetry; High impedance

1. Introduction

Mexico holds the fifth place in production of lead metals worldwide. Galena ore being the most common mineral is associated with some other values treated by froth flotation during the mineral beneficiation processes. Lead grades continues diminishing day after day. However, flotation processes have a great potential to work on those complex ores. Different types of depression reagents are used to shrink lead ores in a selective flotation for complex ores such as Pb–Zn–Cu. Some of those reagents are expensive and may pollute lakes or rivers if they reach high concentrations. Therefore, it is necessary to do research on a clean depressor reagent and know the interaction between PbS–C₆H₈O₅–KEX (galena–dextrine–xanthate) system to obtain an efficient depressor and to preserve a clean environment with a clean reagent. Some studies have been carried out at very specific conditions by different workers [1,2,5–8,10] obtaining reaction products that could be altered in their preparation. Thus, it is important to work with a technique that can be operated in an in situ way, following the solid/solution interface modification of a mineral pulp during a physical chemistry interaction. High frequency impedance (HFI) technique can be used for this purpose, specifically for those non-conductive ores or materials. The present study was undertaken to: (1) determine the responsible reaction products of the flotation and depression of the galena by cyclic voltammetry technique, (2) provide data on the collector and depressor concentrations and mixed reagents, (3) establish the concentration level of depression when the collector occurs with dextrine, (4) determine the suitable collector and depressor concentrations to float and shrink PbS, respectively; all this from HFI studies, (5) apply the best conditions obtained above to float and depress PbS.

2. Experimental procedure

High purity galena ores supplied by Grupo México were characterized by atomic absorption technique and were shaped and cut off to obtain cubes of 1 cm³ to prepare the respective solid work electrodes (PSW) using a diamond disk and mounted after that on a non-conductive cold resin. Galena surface was cleaned after each test by grinding paper no. 600 and raised with distilled water. Cyclic voltammetry studies were carried out on a VersaStat 250 potentiostat/galvanostat and attached to a 486 Acer personal computer with a GPIB board and IEEE386 interface.

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doi:10.1016/S0924-0136(03)00297-8
The scan rate tested was 10 mV/s, with initial potential $E_i = -1300 \text{ mV}$ to switched potential $E_s = 0 \text{ mV}$. Saturated calomel was the reference electrode (SCE).

High impedance technique was used with small crushed and ground PbS samples around $-200 + 400$ mesh with a volumetric fraction of 0.404 and 71.42 wt.% solids. The $Z$ absolute values were transformed to dielectric constant, using a Vector Impedance Meter 4193A Hewlett Packard. The frequency range tested was from 0.5 to 100 MHz. Distilled water was used for all the experiments, and all the reagents were analytical reagent grade. Xanthate and dextrine solutions were buffered with boric acid and sodium borate to obtain a pH of 9.2. The conditioning time for all the samples was 5 min. The recorded values were selected to 100 MHz.

Finally flotation tests were carried out on a Denver lab flotation cell of 1.5 l capacity, 20 wt.% solids, 1100 rpm, and concentrate samples were taken to 20, 40, 60 and 480 s, followed by filtration and dried steps, and analyzed by atomic absorption.

The sequential steps to investigate the above-mentioned variables were: atomic absorption, cyclic voltammetry, HFI and flotation test.

Tables 1 and 2 show the collector and depressor concentration conditions applied on the cyclic voltammetry and HFI, respectively.

### Table 1: Potassium ethyl xanthate and dextrine concentrations used on PbS by cyclic voltammetry technique

<table>
<thead>
<tr>
<th>KEX (M)</th>
<th>Dextrine (ppm)</th>
<th>KEX (M) + dextrine (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>50</td>
<td>0.01 + 50</td>
</tr>
<tr>
<td>0.001</td>
<td>100</td>
<td>0.01 + 100</td>
</tr>
<tr>
<td>0.0001</td>
<td>150</td>
<td>0.01 + 150</td>
</tr>
<tr>
<td>–</td>
<td>0.001 + 50</td>
<td></td>
</tr>
<tr>
<td>–</td>
<td>0.001 + 100</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2: Potassium ethyl xanthate and dextrine concentrations used on PbS by high impedance technique

<table>
<thead>
<tr>
<th>KEX (M)</th>
<th>Dextrine (ppm)</th>
<th>KEX (M) + dextrine (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>50</td>
<td>0.05 + 5</td>
</tr>
<tr>
<td>0.001</td>
<td>10</td>
<td>0.05 + 10</td>
</tr>
<tr>
<td>0.0001</td>
<td>20</td>
<td>0.05 + 20</td>
</tr>
<tr>
<td>–</td>
<td>0.005 + 5</td>
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<tr>
<td>–</td>
<td>0.0005 + 10</td>
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<tr>
<td>–</td>
<td>0.0005 + 20</td>
<td></td>
</tr>
<tr>
<td>–</td>
<td>0.0005 + 30</td>
<td></td>
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</tbody>
</table>

### 3. Results

#### 3.1. Cyclic voltammetry results

For 0.01 M KEX (Fig. 1), the first anodic peak is attributed to lead oxide since high relative potential values promote the oxidation. This type of reaction was reported by Gadner and Woods [3]:

$$\text{Pb} + \text{H}_2\text{O} = \text{PbO} + 2\text{H}^+ + 2\text{e}^- \quad (1)$$

This can be verified by comparing the experimental potential values against theoretical values: $E_{\text{theo}} = -0.846 \text{V}$ and $E_{\text{exp}} = -0.844 \text{V}$. The second peak corresponds to lead xanthate which has been shown by Chemielewski and Lekki [4] with the following reaction:

$$\text{PbS} + 2\text{X}^- = \text{PbX}_2 + \text{S} + 2\text{e}^- \quad (2)$$

where $E_{\text{theo}} = -0.657 \text{V}$ and $E_{\text{exp}} = -0.656 \text{V}$. A third peak was obtained in this voltammogram assuming and adsorbed xanthate. Chemielewski and Lekki [4] explained this product according to the following reaction:

$$2\text{X}^- = 2\text{X}^\text{ads} + 2\text{e}^- \quad (3)$$

Theoretical and experimental potential values for this reaction are: $E_{\text{theo}} = -0.310 \text{V}$ and $E_{\text{exp}} = -0.310 \text{V}$, respectively.
Fig. 2. Voltammogram of the dextrine at pH 9.2, and scan rate of 10 mV/s.

For 0.001 M KEX, almost the same reactions were observed in this system but without any adsorbed species, having for the first peak and Eq. (1): $E_{theo} = -0.846$ V and $E_{exp} = -0.844$ V. For the second peak corresponds Eq. (2), where $E_{theo} = -0.539$ V and $E_{exp} = -0.511$ V. The third observed peak with Eq. (3) has $E_{theo} = -0.250$ V and $E_{exp} = -0.240$ V values.

The lower concentration of potassium ethyl xanthate 0.0001 M showed the first three peaks obtained as above, but the absence of adsorbed xanthate, being the peaks and reactions, was as follows: $E_{theo} = -0.846$ V and $E_{exp} = -0.841$ V for the first peak and first reaction, Eq. (1), $E_{theo} = -0.508$ V and $E_{exp} = -0.496$ V according to Eq. (2). All the experimental potential figures were increased to anodic values as the diminishing ethyl xanthate concentration had a good agreement with the theoretical expected values.

For dextrine (50 ppm)–lead sulfide system (Fig. 2) was observed the reaction product of lead oxide in the first peak and Eq. (1) with $E_{theo} = -0.846$ V and $E_{exp} = -0.840$ V followed by a second peak for the organometallic compound [9] according to the following equation:

$$\text{PbS} + \text{C}_6\text{H}_8\text{O}_5^2^- \rightarrow \text{Pb}_(\text{C}_6\text{H}_8\text{O}_5) + \text{S} + 2\text{e}^-$$  (4)

where $E_{theo} = -0.496$ V and $E_{exp} = -0.497$ V. A third peak was found, and suggesting the presence of thiosulfates according to the following equation:

$$\text{S}_2\text{O}_3^2^- \rightarrow \text{S}_4\text{O}_6^2^- + 2\text{e}^-$$  (5)

with $E_{theo} = -0.240$ V and $E_{exp} = -0.257$ V. Dextrine with 100 and 150 ppm showed the same reactions, i.e. Eqs. (1), (4) and (5) (Fig. 2), where the organometallic compound has less cathodic potentials values as the concentration dextrine is raised: $E_{theo} = -0.505$ V and $E_{exp} = -0.496$ V for 100 ppm and $E_{theo} = -0.510$ V and $E_{exp} = -0.494$ V for 150 ppm.

When xanthate and dextrine were mixed and conditioned with the galena, reaction products are more difficult to assign because of the nearness potential values. Fig. 3 shows the almost coexistence of lead ethyl xanthate and

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Fig. 3. Voltammogram of the dextrine at pH 9.2, and scan rate of 10 mV/s.
the organometallic compound, having very similar potential values (i.e. $E_{\text{exp}} = -506$ V for 50 ppm dextrine + 0.001 M KEX for Eqs. (2) and/or (4) and $E = -0.511$ V for 0.01 M KEX alone, Eq. (2)). This behavior was observed for all the mixed compounds.

Potassium ethyl xanthate concentration effect studied by HFFI shows an isotherm obtained at 100 MHz to find the suitable collector concentration for PbS mineral flotation. It can be observed from Fig. 4 that there is a concentration of KEX ranging from $1 \times 10^{-3}$ to $1 \times 10^{-4}$ M, where the pulp shows the highest change in $\varepsilon'$ permittivity, and constant values for higher collector concentrations. Therefore, it could be assumed that it is not necessary to use higher concentrations than this range ($\varepsilon' = 325$) to float galena ores.

In reference to dextrine–galena system (Fig. 5), there is a rise in $\varepsilon'$ values as the dextrine concentrations were increased to 20 ppm ($\varepsilon' = 560$) opposed to the behavior of collector. Therefore, it can be assumed that there is a chemical adsorption of the PbC$_6$H$_8$O$_5$ organometallic compound and that it is not necessary to operate for concentrations higher than 20 ppm. In Fig. 5, collector concentration effect on PbS–dextrine system can be observed. For the highest collector concentration of 0.05 M KEX, there is an increase in $\varepsilon'$ values, as the dextrine concentration raised is higher than that obtained for the KEX alone and lower than that for the dextrine alone.

Flotation results (Fig. 6) show high concentrate recoveries for the suitable $1 \times 10^{-3}$ M KEX collector with rates and a very significant depression for the galena ore with 20 ppm dextrine. There is a considerable competition between the collector and the depressor having 52% recovery. All these behaviors are expected from the obtained figures from cyclic voltammetry and HFI.

![Fig. 4. Dielectric constant of potassium ethyl xanthate on PbS at pH 9.2 and 100 MHz.](image1)

![Fig. 5. Dielectric constant of dextrine (20 ppm)–potassium ethyl xanthate at pH 9.2 and 100 MHz.](image2)

![Fig. 6. Dielectric constant of dextrine (20 ppm)–potassium ethyl xanthate at pH 9.2 and 100 MHz.](image3)
4. Conclusions

There are good correlations between the high frequency studies and the observed flotation results to float and depress galena ores with potassium ethyl xanthate and dextrine, respectively. Chemical adsorption of both collector and depressor were presented on the galena ore. The assumed organometallic compound obtained by cyclic voltammetry is responsible for depressing PbS.

Acknowledgements

The authors express sincere thanks to Grupo México for the provision of ore samples worked in this research.

References