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Electrochemical Analysis of Galena Reactivity in Typical Physicochemical Conditions of Calcareous Soils

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A proposal methodology using electrochemical techniques and carbon paste electrodes (CPE) were applied to evaluate the oxidation mechanisms of galena and identify secondary species on its surface, in a medium that simulates typical physicochemical environment of the calcareous soils. This study was conducted at the larger interval of potentials, carried out beyond that data reported in the literature. The secondary species were observed with scanning electron microscopy technique. The results showed that with the proposed methodology was possible evaluate to quickly the oxidation mechanisms of galena due to instantaneous formation of secondary phases on the galena mineral surface and a simulated medium. Galena (PbS) mineral is initially oxidized to sulfide intermediate species deficient in metal, followed by formation of a passive film of anglesite ($PbSO_4$). The subsequent formation of cerussite ($PbCO_3$) was carried out mainly by precipitation mechanism; meanwhile an electrochemical oxidation to cerussite occurs when the passive film of anglesite is dissolved from the galena surface. Finally, the formation of compact elongated structures with nanotubes shape was observed (likely phases of PbO_2) to more positive potentials ($E_{\lambda+} \geq 1.8$ V).

Keywords: Galena mineral, electrochemical oxidation, calcareous soils, anglesite, cerussite.

1. INTRODUCTION

Sulfide minerals are dominantly the main sources to extract some important base metals. Galena is the principal sulfide mineral for extraction of lead, but due to some limitations during its separation process, some values of this mineral, unstable, are disposed as mining waste. Due to weathering agents, the alteration of galena mineral is promote and some secondary species were

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generated, depending on the physicochemical environment in contact [1-4]. Several mining sites in Mexico and in the world, where sulfide mineral deposits are extracted, are located in geographic areas with calcareous soils. In these sites, high contamination of soils, sediments and water bodies, by lead and other toxic elements have been identified [4-8]; even under neutral-alkaline carbonated conditions [6, 7]. It has been reported that some of the secondary phases of galena (i.e. $PbCO_3$) present a high bioaccessibility for humans [9], causing health hazards [5-7, 10]. Several studies on the mechanisms of galena oxidation in acid and alkaline media have been conducted [11-19]; however, there is not enough information on the oxidative processes of this mineral in the physicochemical conditions of calcareous soils [19]. It has been reported that galena weathering in carbonated soils produces lead phases such as anglesite, cerussite, hydrocerussite or lead hydroxide [4, 15, 18-19]. However, few studies focus on understanding the stages of the galena oxidation and especially the mechanisms generating secondary species in calcareous soil conditions. Moreover, studies have been performed to describe the processes of galena weathering and the transformation of secondary lead phases occurring on the galena surface (exposed to neutral alkaline-carbonated solutions), using wet mini-cells [18]. Although they combine analysis with chemical and electrochemical techniques, the procedure to collect samples and to get results is lengthy (weeks or months). Furthermore, they considered the presence of some ions of calcareous soils (SO_4^{2-}, $Cl_2^{-,}$ HCO^{3-}, CO_3^{2-}) separately, so that the evolution of the progressive oxidation process and the generated phases is not accessible on the time. On other hand, electrochemical characterization using cyclic voltammetry with carbon paste electrodes (CPE) has been an effective tool in the reactivity study of sulfides [13, 16, 20-21]. Besides, potentiostatic manipulation of the interfacial potential allows modeling of the overall reactivity on the minerals surface [1, 22]. Additionally, the combination of electrochemical and spectroscopic techniques provides an effective approach to elucidate the reaction mechanisms occurring on the mineral surface [13, 22-23]. Hence, this work presents a systematic voltammetric study in a wide range of potential, using carbon paste electrodes (CPE-galena) and an electrolyte that simulate the conditions of calcareous soils. This study is aimed to determine the progressive oxidation process and the mechanisms that generate secondary phases on the galena surface in the less time. Finally, the reaction mechanisms and secondary lead phases generated on the mineral surface were supported by analysis of scanning electron microscopy (SEM/EDS).

2. EXPERIMENTAL

A sample of galena mineral was collected from the mine “El Monte” of the mining district of Zimapan (Mexico). Quartz and sulfide impurities were removed by hand sorting under an optical microscope. The sample was ground in an agate mortar and then it was sieved to <74 μm (-200 mesh size). The mineral was characterized mineralogical and chemically to determine the stoichiometric composition and the contents of mineralogical impurities. The mineralogical phases were determined with SEM/EDS and the chemical content was obtained by inductively coupled plasma (ICP) analysis. Chemical and mineralogical characterization reveals that the sample presents a purity of 94.8% PbS. The solution used to simulate weathering conditions of calcareous soils, was prepared according with data of Table 1. This composition was obtained after analyzing the leaching of calcareous soils samples of the mining district of Zimapan, which were obtained under standard method D3987-85 [24]. This solution used as electrolyte in the electrochemical study was prepared at pH 8 with deionized water; the used reagents ($NaSO_4$, NaCl, $NaHCO_3$, $NaCO_3$) were analytic grade. The electrolytic solution prepared this way was deaerated and preserved with nitrogen atmosphere before and during all the experiments.

Table 1. Ions concentration of the calcareous soils leaching from the mining district of Zimapan.

pH	*C* (mol/L)			
	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}
7.5 – 8.1	0.0187	0.0094	0.059	0.190

In the experimental arrangement, a typical three-electrode cell was used; keeping the atmosphere inert by bubbling nitrogen and at room temperature. A graphite solid bar was used as the auxiliary electrode and a standard sulfate electrode (SSE, $E =$ 615 mV/SHE) immersed in a Luggin capillary, as the reference electrode. Working electrode was prepared mixing carefully the graphite powder and the mineral with silicon oil; later it was homogenized in the agate mortar. The ratio used for graphite powder and mineral (PbS) was 20:80 % wt. The resulting paste (CPE-PbS) was incorporated inside the tube with an apparent surface area exposed to the solution of 0.0314 cm^2. Fresh surface was created for each experiment by extruding the mineral paste and cutting off the spent part. The electrochemical study was carried out using cyclic voltammetry technique with a PAR 263A potentiostat/galvanostat and experimental data was collected with the PowerSuite Software. Voltammetry studies were carried out within the potential range of -1.4 V to 2.0 V vs SHE at a scan rate of 20 mV s^{-1}, starting from the open circuit potential (OCP). All potential values were reported with respect to the standard hydrogen electrode (SHE). In order to simulate the alteration of the galena surface under environment physicochemical conditions of the calcareous soils, controlled potential was applied by 60 seconds to the exposed surface of the CPE-PbS with the electrolyte, using chronoamperometry technique. The potentials applied were selected after a voltammetry study where the different oxidative processes of galena were observed. After the alteration, the CPE-PbS was placed in a desiccator with silica and then vacuum was applied for 6 hours to remove surface moisture. Before characterization by SEM / EDS, the electrode surface is coated with gold in order to better observe the images and the products present at the mineral surface. SEM and EDS studies (images and semi-quantitative elemental microanalysis acquisition) to reveal some secondary species were carried out using a JEOL scanning electron microscope model 6300. This microscope was equipped with an energy dispersive spectrometer detector. Stoichiometry analyses were carried out discounting the oxygen amount from the silicon oil, present in the CPE paste. This was achieved by comparing of SEM and EDS studies carried out on a CPE-mineral without electrochemical modification.

3. RESULTS AND DISCUSSION

3.1 Electrochemical characterization of galena

The electrochemical behavior of CPE-PbS in the electrolytic solution used to simulate weathering under conditions of calcareous soils was carried out in order to identify the stages of oxidation of the galena and to establish the potentials at which the secondary species were generated. The analysis includes the effect of changing the switching positive potential ($E_{\lambda+}$) on global voltammetry behavior, electrochemical alteration and surface characterization.

3.1.1. Voltammetric analysis

Figure 1 shows the voltammetric response of the CPE-PbS electrode in the electrolytic solution used to simulate weathering conditions of calcareous soils, the scans were started in (ii) positive and (iii) negative direction, from the open circuit potential (OCP) at a sweep rate of 20 mV s-1. The electrochemical behavior of the CPE-without mineral (100% graphite) in the positive direction is also shown in Figure 1 (scan i) for comparative purposes. This last one does not show oxidation or reduction representative responses in the whole of potential range where the mineral has its electrochemical response. When the scan potential was initiated in positive direction, a slow oxidation process A1’ was observed between ~0.6 V and 1.1 V, beyond this process, one more oxidation process, A1, was observed. On the reverse scan, an important reduction process, C1, and two more oxidation processes, A2´ and A2 were observed. Meanwhile, when the scan potential was initiated in negative direction, only a small reduction process, C2′, and two oxidation processes, A2” and A1, were observed.

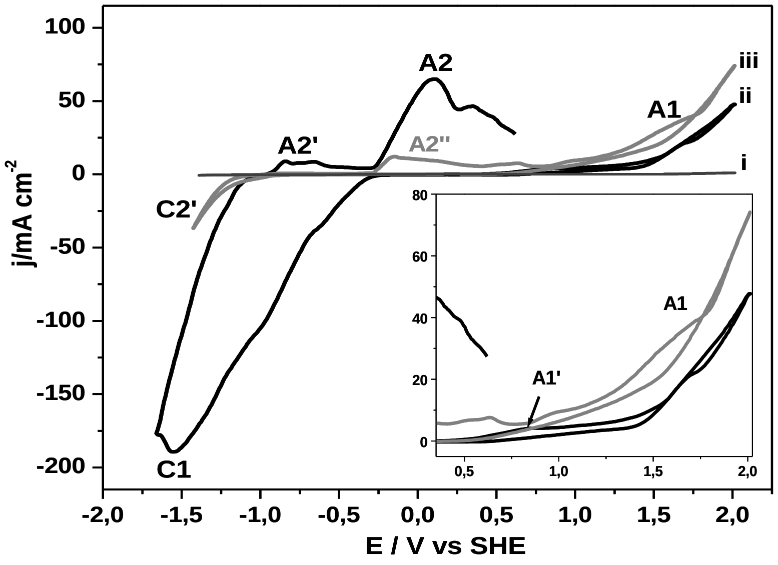

Figure 1. Cyclic voltammograms obtained on (i) CPE-without mineral in positive direction and CPE-PbS (20:80 % wt) when the potential scan was initiated in (ii) positive direction and (iii) negative direction at 20 mV s-1, in a simulated environment of leaching of calcareous soils (pH 8.0).

In order to identify all the products of the surface reactivity of galena and to establish the potentials at which the secondary species were generated, a study varying the positive limit ($E_{\lambda+}$) of switching potentials was carried out, where the negative limit of switching potential was fixed at -1.4 V. According to this study it was possible to distinguish two important stages of galena oxidation, the first step is carried out between 0.6 V and 1.1 V ~ and the second between ~ 1.2 and 2.0 V (Figures 2 and 3, respectively).

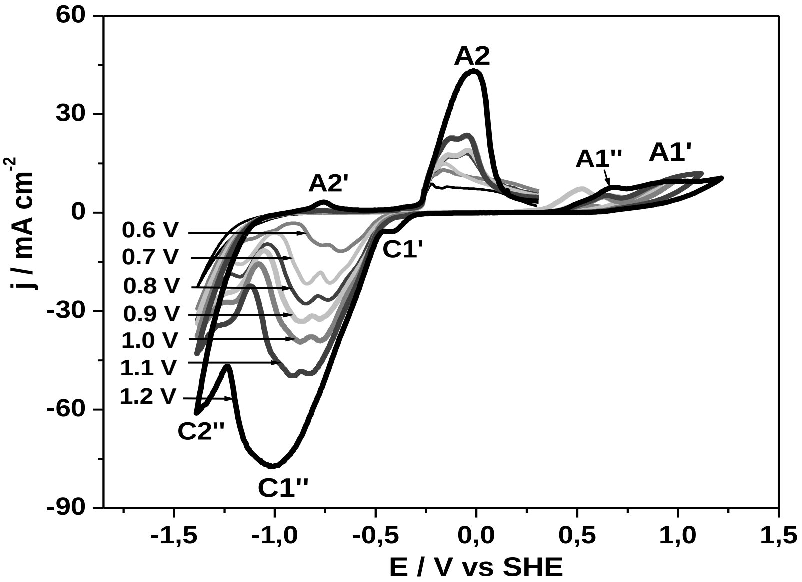

Figure 2. Cyclic voltammograms obtained from a CPE-galena (20:80 % wt) in a simulated environment of leaching of calcareous soils (pH 8.0), the potential scan was initiated on positive direction at 20 mVs-1 and the positive switching potential ($E_{\lambda+}$) was variated between potentials 0.6 < $E_{\lambda+}$ < 1.2 V.

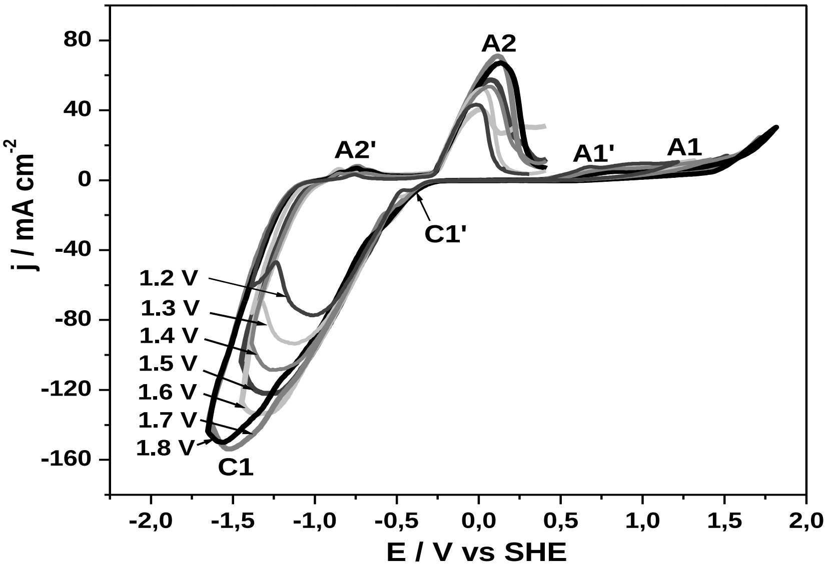

Figure 3. Cyclic voltammograms obtained from a CPE-galena (20:80 % wt) in a simulated environment of leaching of calcareous soils (pH 8.0), the potential scan was initiated on positive direction at 20 mV s-1 and the positive switching potential (Eλ+) was variated between potentials 1.2 < $E_{\lambda+}$ < 1.8 V.

The beginning of the first stage was observed through the formation of a small wave, A1", between 0.4 V and 0.6 V. It can be observed in literature that the oxidation of galena in these potentials has been associated with the generation of sulfide intermediate species partially deficient in metals [25-27], as indicated by the following reactions:

$$PbS \longrightarrow Pb_{1-x}S + xPb^{2+} + 2xe^- \quad (1a)$$

$$xPbS + 4xH_2O \longrightarrow xPb_{1-x}SO_4 + xPb^{2+} + 8xH^+ + 10xe^- \quad (1b)$$

When the switching potential was more positive ($0.6\ V \leq E_{\lambda+} \leq 1.1\ V$), a slow oxidation process A1’ was observed, which reached a maximum (at ~ 0.9V), and then decreased slowly. This behavior has been generally associated to the formation of a passive film on the electrode surface of sulfides [12, 16, 20-21]; in this case probably sulfate or metal hydroxides. Due to the important amount of sulfate ions occurring under the interfacial equilibrium conditions in calcareous soils and the pH value under study, is likely that the formation of anglesite takes place, according with the following reactions [13, 16, 18]:

$$PbS + 4H_2O \longrightarrow PbSO_4 + 8H^+ + 8e^- \quad (2a)$$

$$PbS + SO_4^{2-} + \tfrac{2}{3}H_2O \longrightarrow PbSO_4 + \tfrac{1}{2}S_2O_3^{2-} + 3H^+ + 4e^- \quad (2b)$$

At this stage, the phase formation of $Pb(OH)_2$ was not considered because this species is believed kinetically limited during its formation at low potentials and under the conditions in which the electrochemical experiments were carried out [13, 15]. This fact was also supported by an analysis of the cathodic zone (Figure 2), which showed that the current associated with process C1’’ began to increase at $E_{\lambda+} \geq 0.6$ V. Meanwhile process C2’’, is enhanced at $E_{\lambda+} \geq 0.5$ V. Thus, peaks C1’’ and C2’’, have been associated to the reduction of $PbSO_4$ and galena mineral to elemental lead, according to the reactions 3a and 3b, respectively [14, 16].

$$PbSO_4 + 2e^- \longrightarrow Pb^0 + SO_4^{2-} \quad (3a)$$

$$PbS + 2H_2O + 2e- \longrightarrow Pb^0 + H_2S + 2OH^- \quad (3b)$$

At potentials of $E_{\lambda+}$ between 1.2 V and 1.8 V, a steadily rise in current for the reduction process, C1, was observed (Figure 3), indicating the beginning of the second stage of the mineral oxidation. This fact was attributed to the destabilization of the passive film of anglesite formed at anodic potentials due to the presence of hydrogen and HCO^{3-} ions on the interface. However, a slow growth of the oxidation process, A1, at these potentials, relative to the reduction process, C1, was observed (see Figure 3). This indicates that the formation of the new secondary specie on the electrode surface (CPE-galena) was mainly due to a chemical deposition process. The expected secondary specie that may form at these potentials due to the neutral-alkaline conditions of the electrolyte and presence of carbonate ions is the cerussite ($PbCO_3$). However, the transformation process of anglesite to cerussite may involve direct reaction with carbonates or hydrolysis and subsequent precipitation on the surface of the mineral, with diffusion of species through cerussite pores [18]. Thus, the mechanisms proposed in the formation of cerussite was according some of the following reactions:

$$PbSO_4 + CO_3^{2-} \longrightarrow PbCO_3 + SO_4^{2-} \qquad \Delta G^o_{298} = -29.2\ kJ\ mol^{-1} \quad (4a)$$

$$PbSO_4 + 3OH^- \longrightarrow Pb(OH)_3^- + SO_4^{2-} \qquad \Delta G^o_{298} = -35.23\ kJ\ mol^{-1} \quad (4b)$$

$$Pb(OH)_3^- + HCO_3^{2-} \longrightarrow PbCO_3 + 2OH^- + H_2O \qquad \Delta G^o_{298} = -14.87\ kJ\ mol^{-1} \quad (4c)$$

After that, the passive film of anglesite is dissolved on galena surface; this progressively reacts electrochemically according to reaction 5.

$$PbS + CO_3^{2-} + 4H_2O \longleftrightarrow PbCO_3 + SO_4^{2-} + 8H^+ + 8e^- \quad (5)$$

The above was also supported by a study of the integration of cathodic and anodic charges of Figures 2 and 3 (see Table 2 and chart in Figure 4) that produced an increase of charge ratio, QA/QC, between the potentials of 0.6 to 1.1 V and decreased, on the potentials 1.2 to 1.8 V. This fact confirms the dissolution of the anglesite film (reactions 4a-c) and the electrochemical reaction of the galena surface to cerussite (reaction 5).

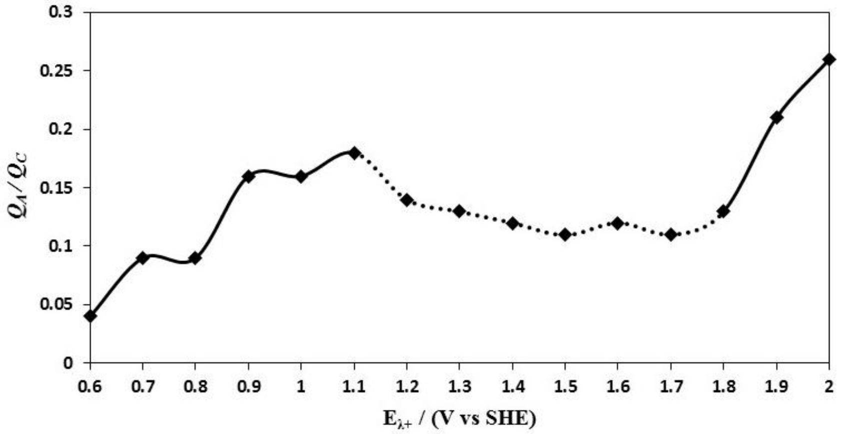

Figure 4. Evolution of ratio charges on a CPE-Galena obtained from different positive switching potential (Eλ+) voltammetries.

Table 2. Cathodic, anodic and ratio charges obtained from different positive switching potential voltammetries.

$E_{\lambda+}$ (V vs SHE)	Q_A *(mC)* A1" + A1' +A1	Q_C *(mC)* C1" +C2" (C1' + C1)	Q_A/Q_C
0.6	0.75	19.78	0.04
0.7	2.53	28.06	0.09
0.8	3.06	34.22	0.09
0.9	6.36	40.3	0.16
1	7.73	47.1	0.16
1.1	10.39	58.1	0.18
1.2	12.77	89.52	0.14
1.3	14.37	110.4	0.13
1.4	15.23	128.3	0.12
1.5	17.24	154.4	0.11
1.6	19.68	165	0.12
1.7	26.08	228.1	0.11
1.8	29.51	223.8	0.13
1.9	54.24	262	0.21
2	82.01	315.5	0.26

Moreover, the process, C1, was associated with a reduction of cerussite to metallic lead, according to the reactions 6a-b. While the reduction process, C1 ', was associated with the reverse reaction 5, where the resulting species (PbS) would be reduced to elemental lead in the process C1, according to reaction 3b.

$PbCO_3 + H_2O + 2e^- \longrightarrow Pb^0 + HCO_3^- + OH^-$ (6a)

$PbCO_3 + 2e^- \longrightarrow Pb^0 + CO_3^{2-}$ (6b)

To more anodic potentials ($E_{\lambda+} \geq 1.8V$) a greater oxidative activity of the galena can be observed, since the oxidation process, A1, appears with a higher current density (Figure 3); besides the increase in charge ratio, Q_A/Q_C, at these potentials (see Figure 4 and Table 2). This activity is mainly associated with the formation of secondary species of lead oxide (i.e. PbO_2) which is formed from the direct oxidation of the mineral and cerussite oxidation, according to reactions 7a-b.

$PbS + 6H_2O \longrightarrow PbO_2 + SO_4^{2-} + 12H^+ + 10e^-$ (7a)

$PbCO_3 + 2OH^- \longrightarrow PbO_2 + CO_3^{2-} + 2H^+ + 2e^-$ (7b)

Finally, the resulting oxidized species of lead (PbO_2), is reduced to metallic lead in the reduction process, C1, according to reaction 8.

$PbO_2 + 2H+ + 2e^- \longrightarrow Pb^0 + H_2O$ (8)

3.1.2. Electrochemical alteration and characterization of surface

SEM and EDS studies were performed on the CPE-galena surfaces, before and after being altered electrochemically for 60 seconds in an electrolyte that simulated conditions of calcareous soils, at an oxidation potential of 0.78 V (Figure 5a and 5b, respectively), corresponding to the wave, A1'.

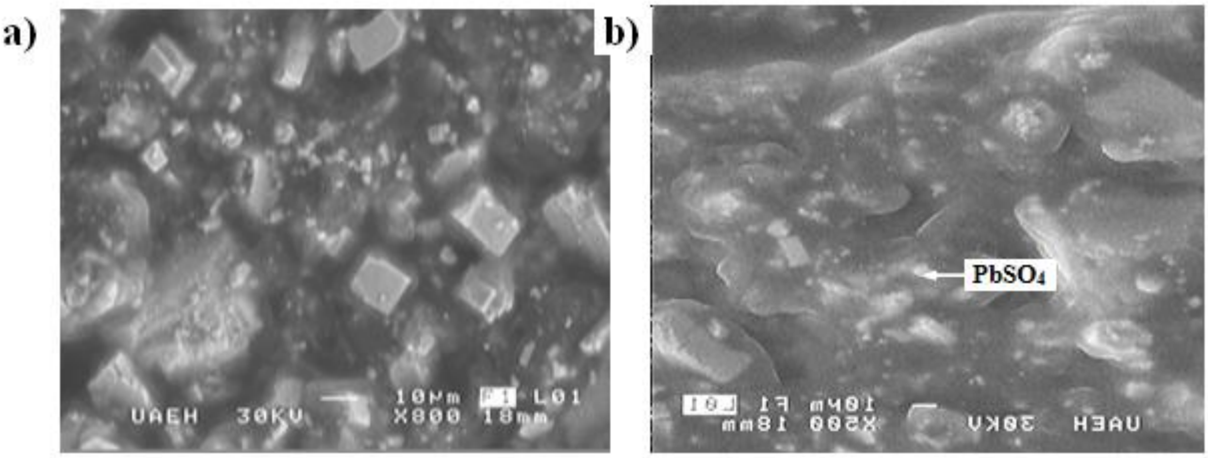

Figure 5. SEM images obtained on the surface of a CPE-galena, a) before altering electrochemically and b) after electrochemical alteration in a simulated environment of leaching of calcareous soils (pH 8.0) at an oxidation potential of 0.8V during 60 s.

The analysis of the results allowed observing the formation of a film covering the altered surface of the electrode. According to the stoichiometry, and in addition to the structure and form of this film that has been reported in the literature [16, 18], coincides with the secondary specie of anglesite ($PbSO_4$), the results also are consistent with the reactions 2a and 2b. Figure 6 shows the SEM/EDS study performed on electrochemically altered surface of a CPE-galena, when an oxidation potential of 1.1 V is imposed and followed by the imposition of a reduction potential of -1.08 V, corresponding to the process C1" of Fig. 2. The results revealed the presence of metallic lead by increasing the amount of lead in the semi-quantitative chemical analysis (Table 3), which is according to the reaction 3a [14, 16].

Table 3. Percentage of elements (% wt) obtained by EDS semiquantitative analysis on the surfaces of the CPE-galena mineral electrochemically modified.

	Element (% wt)				
	0.78 V A1'	1.2 V A1	-1.1 V* C1''	-1.34 V** C1	1.8 V A1
Pb	52.12	54.58	67.32	70.32	52.13
S	9.50	6.69	6.83	2.23	3.58
O	32.20	30.26	21.47	18.19	38.47
C	6.18	8.47	8.97	8.31	5.82

* Previously an oxidation potential of 1.2 V during 60 s is imposed.
** Previously an oxidation potential of 1.8 V during 60 s is imposed.

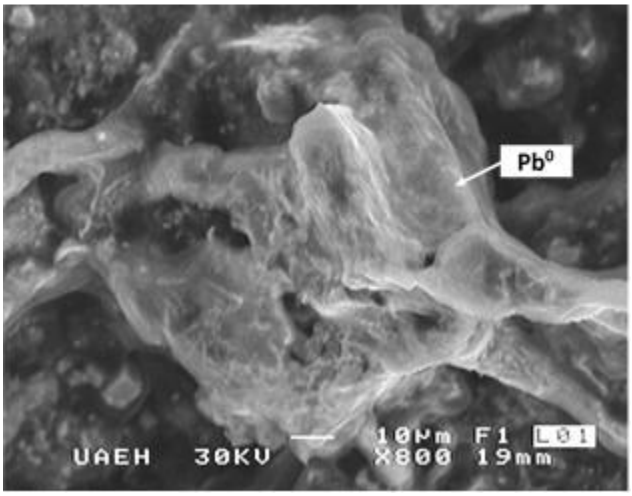

Figure 6. SEM image obtained on the surface of a CPE-galena after imposition of an oxidation potential of 1.1 V during 60 s and followed by the imposition of a reduction potential of -1.08 V during 60 s, in a simulated environment of leaching of calcareous soils (pH 8.0).

When an oxidation potential of 1.2 V is imposed on the galena surface (corresponding to the process A1, in Figure 3) and the altered surface in a simulated environment of leaching of calcareous soils is analyzed by SEM/EDS, it is observed that the anglesite ($PbSO_4$) film that covered the surface of the electrode was dissolved to form a new secondary species. Such species exhibited reticular structures similar to the cerussite with an acicular porous shape (see Figure 7). The stoichiometry and data reported in the literature [18], confirms that this species indicates the presence of cerussite ($PbCO_3$), which is also concording with some of the reactions 4(a-c) and 5.

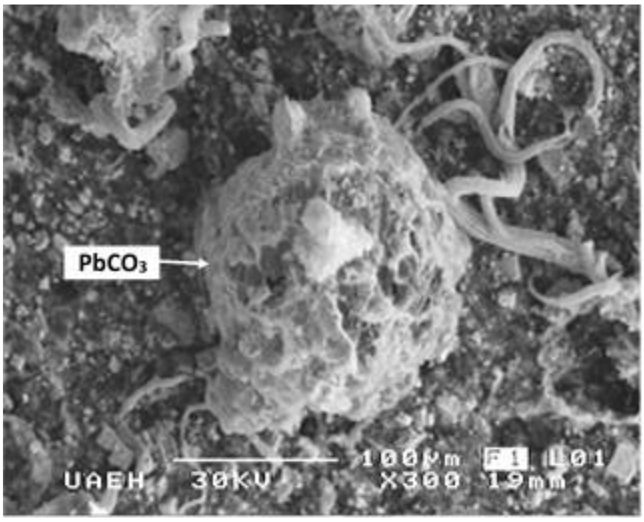

Figure 7. SEM image obtained on the surface of a CPE-galena after the imposition of an oxidation potential of 1.2 V during 60 s, in a simulated environment of leaching of calcareous soils (pH 8.0).

Figure 8 shows the SEM/EDS study on the surface of a CPE-galena altered electrochemically using an oxidation potential of 1.2 V followed by the imposition of a reduction potential of -1.1V; corresponding to the reduction process C1 in figure 3. Results obtained corroborated the reduction to metallic lead, which is supported by the stoichiometry increasing the lead content on the semiquantitative chemical analysis by EDS (see Table 3). This is also concordant with some of the reactions 6a-b. In contrast, figure 9 shows the SEM/EDS studies on the electrochemically altered surface of a CPE-galena using an oxidation potential of 1.8 V; corresponding to the oxidation process A1 in figure 3. This image shows the presence of elongated species with nanotubes shaped, which has not been reported in the literature.

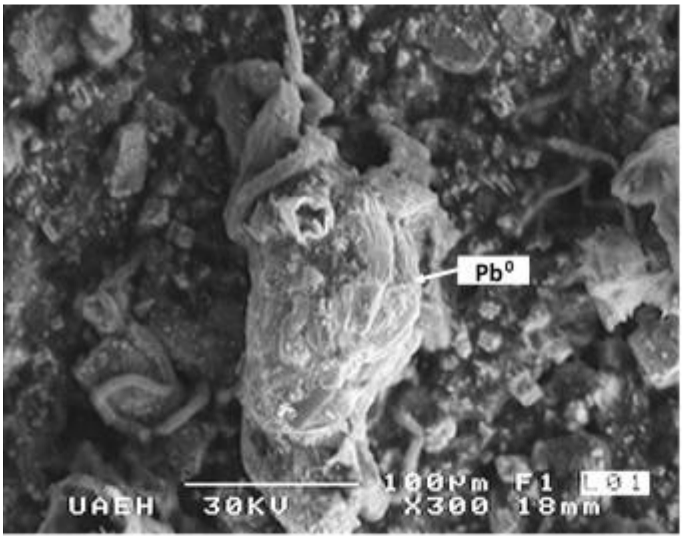

Figure 8. SEM image obtained on the surface of a CPE-galena after the imposition of an oxidation potential of 1.2 V during 60 s and followed by the imposition of a reduction potential of -1.08 V during 60 s, in a simulated environment of leaching of calcareous soils (pH 8.0).

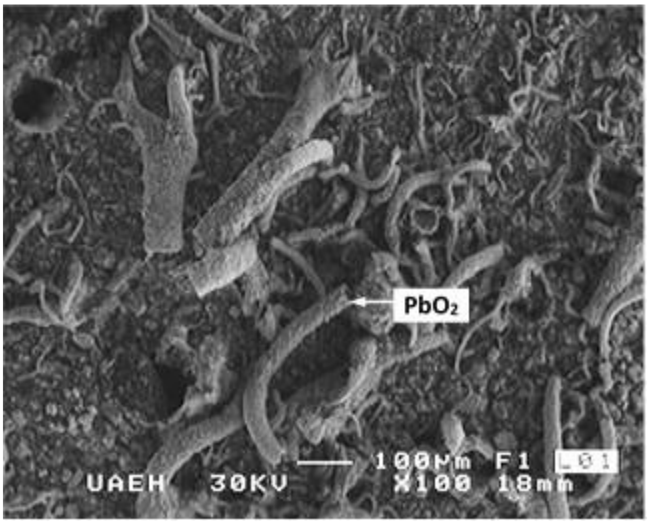

Figure 9. SEM image obtained on the surface of a CPE-galena after the imposition of an oxidation potential of 1.8 V during 60 s, in a simulated environment of leaching of calcareous soils (pH 8.0).

According to the stoichiometry, it is likely that this secondary species corresponds to PbO_2, when the oxygen quantity increases at the used potentials, which is concordant with the reactions 7a-b.

Finally, SEM/EDS analysis to the electrochemically altered surface of a CPE-galena, when imposing an oxidation potential of 1.8 V, followed by a reduction potential of -1.5 V (process C1), shows the same elongated shapes formed at 1.8 V (process A1); which apparently not were dissolved completely according to the reaction 8 (see Figure 9).

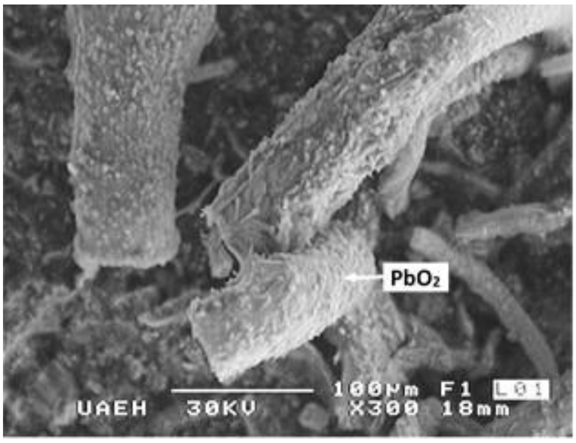

Figure 10. SEM image obtained on the surface of a CPE-galena after the imposition of an oxidation potential of 1.8 V during 60 s and followed by the imposition of a reduction potential of -1.5 V during 60 s, in a simulated environment of leaching of calcareous soils (pH 8.0).

It is important to note that the oxidized species of galena obtained (anglesite and cerussite) agree with the results obtained by the traditional methodology of wet mini-cells and massive electrodes reported in the literature. This indicates that it is possible to use this alternative methodology proposed to study the process of galena weathering under the conditions of calcareous soils.

4. CONCLUSIONS

With the proposed methodology was possible to analyze the reaction mechanisms involved in the progressive oxidation of galena. The results showed that galena is initially oxidized to sulfide intermediate species that are partially deficient in metals, followed by formation of anglesite. The subsequent formation of cerussite (which has an acicular porous shape) was carried out mainly by the precipitation mechanism; while the electrochemically progressive oxidation to cerussite occurs when the passive film of anglesite is dissolved of the galena surface with diffusion of species through cerussite pores. Finally, it was possible to observe the formation of elongated compact structures as nanotubes shaped (probably phases of PbO_2) at more positive potentials ($E_{\lambda+} \geq 1.8$ V), which has not been reported in the literature. It is important to note that the proposed methodology provides results consistent with the results that have been obtained in wet cells and massive electrodes but in less time (≤ 60 sec). This is because the proposed methodology allows the instantaneous formation of secondary phases on the galena mineral surface under simulated physicochemical conditions of calcareous soils.

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