Electrochemical reactivation of galena surface during its electrodissolution in perchlorate medium at pH 0

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Several studies have been carried out on the anodic dissolution of galena concentrates; however, the passivation for the sulfur anodically produced on a galena surface[1-4] has discarded it as an alternative leaching process on an industrial scale.

A previous study[2] showed that in a perchlorate medium at pH = 0, the oxidation of galena takes place according to the reaction ($PbS \rightarrow S^0 + Pb^{2+} + 2e^-$) at $0.50 \leq E \leq 0.60$ V vs. SCE and that at $E > 0.60$ V vs. SCE, galena oxidizes to thiosulfates and sulfates.

The electrochemical methodology proposed to reactivate the surface of this ore concentrate during its dissolution is the potential pulse electrolysis. The experiments were made on CPE-galena in 1.0 M $HClO_4$ using 1.0 M $NaClO_4$ as supporting electrolyte.

The following methodology was employed:

I) A potential pulse of E_{ap1} = 0.56 V is imposed for 180 seconds to form S ($PbS \rightarrow S^0 + Pb^{2+} + 2e^-$).
II) Then, the potential is reversed back to a value of E_{ap2} = –0.60 V for 180 seconds to reduce elemental sulfur ($S^0 + 2H^+ + 2e^- \rightarrow H_2S_{(aq)}$).
III) Once the step I or successively I and II are performed, this electrode is rinsed with deionized water and relaxed for 30 s in the cell with freshly prepared electrolyte solution.
(IV) Immediately after the step III, the voltammogram is traced.

Fig. 1 shows four voltammograms traced in the positive direction on CPE-galena in the unstirred electrolyte. Fig. 1a displays the voltammogram on fresh galena. Fig. 1b shows the voltammogram characteristic of the galena surface after being submitted to electrolysis at E = 0.56 V (forming elemental sulfur) during 180s. Fig. 1c shows the voltammogram characteristic of the final surface condition after double potential step. Fig. 1d will be discussed below.

The anodic currents obtained in the voltammogram of Fig. 1b were lower than those obtained on fresh galena, Fig. 1a. These low currents are attributed to oxidation of the elemental sulfur film that is passive[2].

The voltammogram of Fig. 1c shows the appearance of a pre-wave, (F'), within $0.1 \leq E \leq 0.55$ V prior to the associated processes in (A'). This pre-wave was not detected in Figs. 3a-b. Furthermore, the current associated with (F') was greater than that obtained in the presence of elemental sulfur, Fig. 1b. On the other hand, (F') was detected in a similar study with stirred electrolyte solution (not shown herein). The electrochemical reaction that might be taking place in (F') can be described as[5-6]:

$$PbO_{(s)} + H_2O \rightarrow PbO_{2(s)} + 2H^+ + 2e^-$$

To prevent formation of $PbO_{2(s)}$ (not favorable to galena electrodissolution), anodic behavior of this concentrate (not shown herein) was studied in either 2 M $HClO_4$ or 0.01 M EDTA at pH = 2. However, the formation of lead dioxides was unavoidable. To show the possibility of continuous electrodissolution of galena a double potential pulse program looped consecutively four times was employed. The selected medium was 1.0 M $HClO_4$, since it facilitates electrodissolution better than other studied media.

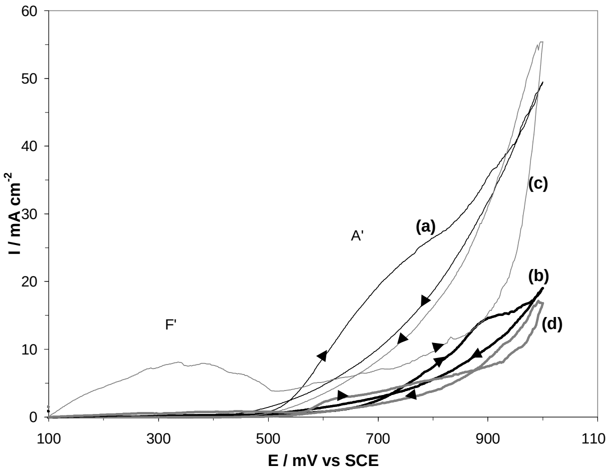

Figure 1. Typical cyclic voltammograms obtained on modified CPE-galena 80:20 wt.% in 1.0 M $HClO_4$ (υ = 100 mV s^{-1}). The modified electrode was rinsed out and then dipped into the freshly electrolyte. The potential scan was initiated in positive direction. The solution was relaxed during 30 s before the potential scan. Unstirred solution. The CPE-galena was submitted to a previous electrolysis: (b) E_{app1} = 0.56 V, t = 180 s; (c) one cycle, E_{app1} = 0.56 and E_{app2} = -0.60 V for 180 s at each applied potential; (d) four cycles, E_{app1} = 0.56 and E_{app2} = -0.60 V for 180 s at each applied potential, and they were compared with one traced on fresh galena, (a).

Fig. 1d show voltammogram characteristic of the final surface condition of the galena following the four times looped double potential step program.

What is noteworthy in the voltammogram traced in the positive direction after four double potential pulse experiments (Fig. 1d) is that the process (F') finally. The disappearance of $PbO_{(s)}$ might be due to its dissolution during reverse pulses of electrolysis. In addition, no elemental sulfur was detected either. The anodic current of the voltammogram in Fig. 1d was much lower than that obtained on fresh galena (Fig. 1a). It suggests that the galena might have been depleted at the electrode surface during the potential pulse program.

SEM-EDX characterization studies of the final surface condition of galena after electrolysis (not show herein) demonstrated the successful reactivation of galena. This is in accordance with the electrochemically obtained findings on CPE-galena.

In conclusion, the galena surface could be reactivated for its continuous oxidation through double potential pulse program looped consecutively four times. The results obtained in this work open up interesting prospects for achieving an efficient quantitative electrorecovery of lead from massive galena ores.

References

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