

Electrochemical contribution of pyrite in arsenopyrite reactivity

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Pyrite (FeS₂) and arsenopyrite (FeAsS) are common sulfide minerals in base metals and precious metals ores and concentrates. The treatment of this kind of ores involves frequently an oxidation stage to improve metal recoveries [1,2]. Besides, the oxidation of these sulfide mineral residues, generates acid mine drainage during weathering [1,3]. The electrochemical characterization using cyclic voltammetry with carbon paste electrodes containing mineral particles (CPE-Mineral) has been an effective tool to demonstrate the overall reactivity of the minerals, at the last decade. In this work, a comparative voltammetric study has been performed on a high purity pyrite mineral (98.8%) and arsenopyrite mineral (content of 86.95% arsenopyrite, 11.84% pyrite), in order to identify the dissolution processes involved on arsenopyrite mineral. This study shows the coexistence effect of minerals, both arsenopyrite and pyrite, and its repercussion on their reactivity. Here cyclic voltammetry technique was used with CPE containing minerals and 0.1M NaNO₃ solution (pH 6.5), as electrolyte. The voltammetric response for CPE-pyrite or arsenopyrite electrodes were obtained on positive and negative direction scans, beginning from open circuit potential (OCP). The potential range was between $-2.0 \leq E \leq 1.4$ V with a scan rate of 0.02 Vs⁻¹.

Cyclic voltammetry on the electrodes shows several oxidation and reduction process. The voltammetric response depends on the initial direction of the scan potential, because some processes are related to the electrochemical oxidation of the mineral.

The behavior of the anodic peaks in the pyrite has been widely studied for several authors. These peaks have been associated with the oxidation of the iron sulfides to form oxy-sulfur species (S_xO_y²⁻), S⁰ and Fe(II and III) species [3,5,6]. On the reverse scan, the first reduction peak (at 0 V vs SSE) is associated with the reduction of oxidized species of iron to ferric hydroxides [3,6]. Moreover, in order to identify the processes involved with the pyrite and arsenopyrite oxidation, a study of anodic inversion on the CPE-arsenopyrite electrode was carried out. In this study, the inversion potential was varied in the positive direction, where the oxidation of mineral was observed ($E_{\lambda+} = 0.4$ to 1.2 V), keeping the negative inversion potential fixed in -2.0 V, the study is shown in the Figure 1. According to literature, it is suggested that arsenopyrite is initially oxidized to realgar (As₂S₂) and Fe(II) in acidic media. Once these species are formed at the interface, the oxidation of As₂S₂ to As₂S₃ can be found to a more anodic potential. Then, the second stage of the oxidation process could be associated to the oxidation of Fe(II) to Fe(III). In the reverse scan, the first reduction peak (G1) is associated with the reduction of oxidized species of iron to ferric hydroxides [3,6], like pyrite.

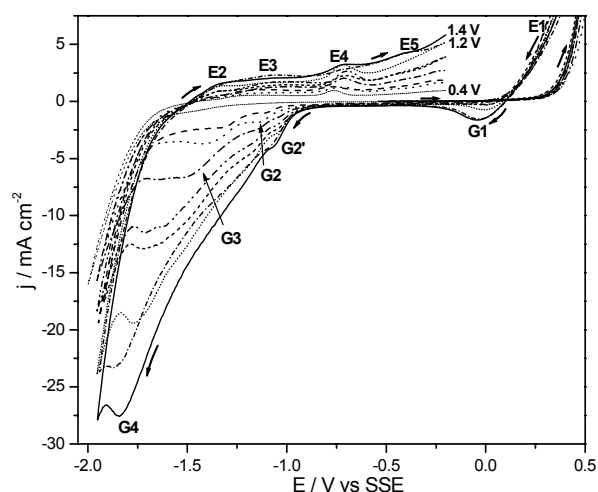
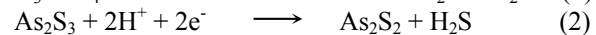
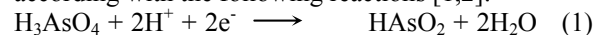
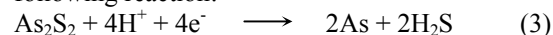


Fig. 2. Typical cyclic voltammograms obtained on CPE-arsenopyrite mineral 20:80 wt% in 0.1 M NaNO₃ at pH 6.5 ($\nu = 20$ mV s⁻¹). The potential scan was initiated in positive direction and the positive switching potential ($E_{\lambda+}$) was varied $0.4 \leq E_{\lambda+} \leq 1.4$ V. The negative switching potential was fixed at -1.8 V.

On the other hand, toward more negative potentials, peak G2, corresponds to the reduction process of As(V) species (formed in the forward scan) to As(III), while peak G3 corresponds to reduction of As₂S₂; according with the following reactions [1,2]:



Therefore, the electrochemical process, G4, is attributed to reduction of realgar, according the following reaction:



A comparison between reactivity with higher purity pyrite and an arsenopyrite mineral, shows that the pyrite is more reactive in the pure pyrite mineral than in the arsenopyrite mineral. Besides, it shows that arsenopyrite mineral is oxidized at less positive potentials than higher purity pyrite (0.1V). On other hand, pyrite in the arsenopyrite mineral has an important contribution in voltammetric response of arsenopyrite mineral, mainly observed in the reduction peak G1 and oxidation peaks E2, E3 and E5 (at $E_{\lambda+} > 1.2$ V).

Results obtained show that in arsenopyrite mineral, electrochemical reactivity of the pyrite was diminished and displaced to more positive potentials respect to the response of high purity pyrite. This behavior can be attributed to the galvanic protection offered by the arsenopyrite to the pyrite, avoiding its free oxidation.

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