

## Electrochemical reactions of arsenopyrite in acidic solutions

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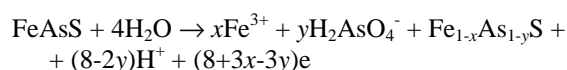
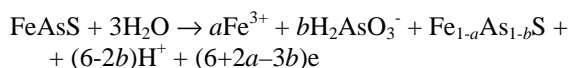
Electrochemistry and surface chemistry of arsenopyrite are poorly studied despite the importance of FeAsS reactivity for recovery of gold and in connection with the environmental problems. In this work, cyclic voltammetry of compact electrodes from natural FeAsS in hydrochloric, sulfuric and nitric acid electrolytes has been examined before and after electrochemical polarization, either cathodic or anodic, as well as after leaching with relevant ferric salt solutions. The reacted surfaces were examined using XPS and X-ray spectroscopy.

Anodic current density is low at potentials below 0.6-0.7 V (vs. Ag/AgCl) and rise at higher potentials. Two cathodic maxima at approximately 0.15 and -0.25 V are observed at the negative-going sweep, they are typical for many sulfide minerals. The curves were fairly similar in various acids, with the current magnitude being somewhat less in sulfate electrolyte. Preliminary cathodic polarization at -0.3 V for 1 h results in a notable increase in the current value during both positive-going potential sweep and the following negative-going scan; the increase was lower in the sulfuric acid medium. After the electrode has been oxidized at 0.6 V, both cathodic and anodic currents drop, with the effect being minimum in the case of sulfuric acid.

In Fe<sup>3+</sup>-bearing acidic electrolytes, the highest current of ferric ion reduction takes place in nitric acid, while the lowest one is in sulfate electrolyte. The cathodic current densities decrease at the second negative-going sweep, excepting the sulfate media. The preliminary leaching in the ferric salt solutions causes essentially lower passivation of arsenopyrite than the electrochemical oxidation.

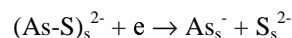
The surface composition of FeAsS electrodes has been found to alter drastically due to the chemical or the electrochemical treatment (Table 1). The arsenopyrite surface is rather oxidized after abrasion in air. After the arsenopyrite has been polarized in the negative-going sweep to -0.3 V, the quantities of oxidized species of iron and arsenic increased, whereas the surface concentration of sulfur diminished and a share of monosulfide species increased. The arsenopyrite oxidized in the sweep to 0.6 V and 0.9 V in 1 M HCl shows progressively increasing amounts of surface Fe<sup>3+</sup>-O and As-O species and decreasing S/Fe and S/As atomic ratios in a non-stoichiometric layer of the sulfide phase. The composition close to Fe<sub>0.3</sub>As<sub>0.4</sub>S has been specified for the electrode oxidized in the sweep to 0.9 V and for ground mineral conditioned in 0.2 M FeCl<sub>3</sub> + 1 M HCl for 1 h, but in the last case the quantity of the oxidized Fe and As species was small. No arsenic phases like As<sub>2</sub>S<sub>2</sub> or As<sub>2</sub>S<sub>3</sub> were determined.

Two stages of the oxidation which differ in a measure of the depletion in Fe and As can be described by conventional reactions



where  $a, b < x, y$ . One can suggest therefore that the less non-stoichiometric layer has a stronger passivation effect as compared with the one with higher excess of sulfur.

The cathodic reduction of arsenopyrite involves a split of As-S bonds in the solid



A part of monosulfide species produced is released then as H<sub>2</sub>S; As<sub>s</sub><sup>-</sup> species are easily oxidized, possibly ex situ.

Table 1. Surface composition of reacted arsenopyrite

| Samples                                  | Atomic ratios |      |
|------------------------------------------|---------------|------|
|                                          | Fe/S          | As/S |
| abraded                                  | 1.13          | 1.53 |
| polarized to -0.3 V                      | 1.04          | 1.43 |
| polarized to 0.6 V                       | 0.72          | 0.93 |
| polarized to 0.9 V                       | 0.50          | 0.94 |
| leached in 1M HCl+0.2M FeCl <sub>3</sub> | 0.30          | 0.41 |

### Acknowledgement

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