Electrochemical Behaviour and Surface Characterisation of Enargite (Cu_3AsS_4) in Acidic Solutions

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The electrochemical oxidation and reduction of the surface of natural enargite (Cu_3AsS_4), has been investigated in 0.1 M HCl solution, using electrochemical kinetic techniques, with subsequent surface analysis by in-situ Raman spectroscopy and X-ray photoelectron spectroscopy (XPS), together with aqueous phase analysis by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Cyclic voltammetry was used to characterise the electrochemical behaviour of the minerals. Chronoamperometric experiments were carried out at a range of potentials, in conjunction with in-situ Raman spectroscopy and ICP analysis, after 500 and 1000 seconds, respectively. Surface analysis showed that elemental sulphur and sulfate were formed when the electrode was polarised at positive potentials. The XPS analyses indicated the presence of $Cu(OH)_2$ and $CuCl_2$ on the surface at potentials > 0 V (SCE). At potential < 0.6 V (SCE), H_3AsO_3 was detected, with As^V forming at higher potentials. Analysis of the electrolyte in contact with enargite showed that the amount of dissolved sulphur increased at both negative potentials, due to reduction to H_2S, and under oxidising potentials, due to the formation of sulfoxy species. The amount of dissolved copper increased at potentials > 0.2 V, whereas dissolved arsenic concentrations were negligible over the entire potential range investigated. A mechanism for the oxidation and passivation of the mineral is proposed, involving the sequential reactions:

$$\begin{aligned} &2Cu_3AsS_4 + 8xH_2O \\ &\rightarrow 2Cu_3As_{1-x}S_4 + 2xH_2AsO_4^- + 12xH^+ + 10xe^- \end{aligned} \qquad [1]$$

$$\begin{aligned} &2Cu_3As_{1-x}S_4 + (28-20x)H_2O \\ &\rightarrow (1-x)Cu_3(AsO_4)_2 + 3(1+x)CuS \\ &+(5-3x)SO_4^{2-} + 2(28-20x)H^+ + (46-34x)e^- \end{aligned} \qquad [2]$$

$$\begin{aligned} &3(1+x)CuS \\ &\rightarrow 3(1+x)Cu^{2+} + 3(1+x)S + 6(1+x)e^- \end{aligned} \qquad [3]$$