Electrochemical Investigation and Surface Characterisation of Tetrahedrite (Cu$_{12}$As$_4$S$_{13}$) in Acidic Solutions

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The electrochemical oxidation and reduction of the surface of natural tetrahedrite (Cu$_{12}$As$_4$S$_{13}$) has been investigated in 0.1 M HCl solution using electrochemical 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. The surface analysis showed that elemental sulphur is formed on the surface when the electrode is polarised at positive potentials. The Raman spectra of tetrahedrite showed that elemental sulfur was detected on the electrode surface only at potentials > 1 V (SCE), at least for the charge densities passed after 500 s. At potentials below 0 V (SCE), no sulfur was observed, but the intensities of the characteristic Raman spectra decreased as the electrode potential was made more negative, due to the dissolution of sulfur as H$_2$S and antimony as AsH$_3$, leaving elemental copper accumulating on the surface.