

Spectroelectrochemical investigation of chalcopyrite oxidation

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Reasonable copper yields from chalcopyrite using sulfate solutions (preferred due to easier impurity management and electrowinning) are not attainable in a practical residence time unless the leaching temperature exceeds 200°C (oxygen pressure leaching) or chalcopyrite is 'activated' by a pretreatment method prior to leaching [1]. A metal-deficient passivating layer on the surface is believed responsible for the poor yields. The oxidative product layer composition and mechanisms by which it forms are not yet fully understood.

A variety of techniques have been used to investigate the nature of the passivating layer formed on chalcopyrite, the most popular being XPS, although SIMS, SEM and AES have also been frequently employed. The high vacuum requirements of these techniques are not ideal for systems where thin sulfur product layers may be present on the mineral surface. Potentiodynamic techniques have been frequently employed to study surface processes *in situ*, and have been usefully employed in conjunction with spectroscopic techniques to provide complimentary data.

Normal Raman techniques used by the present authors indicate that the oxidation product/s of chalcopyrite leached with ferric sulfate solutions are not rhombic sulfur. Bands consistent with S-S stretching vibrations in the absence of bending modes were observed, indicating sulfur pairs or constrained chains or rings, though the stretching frequency was substantially lower than that reported for a ring structure. *In situ* observations of the chalcopyrite surface under potential control in HCl solutions indicated that a Raman inactive product phase was formed that was activated under the laser to form a Raman active phase containing sulfur-sulfur bonds. Rhombic sulfur was the major product at potentials in the main anodic wave region ($E > 0.700$ mV/Ag/AgCl) or at elevated temperatures.

Thin passivating layers formed on sulfides, and initial reaction products, would not be discernible by Normal Raman spectroscopy. However, surface enhanced Raman scattering (SERS), which occurs with roughened coinage and alkali metal surfaces can reveal monolayer, or even single molecules under the right conditions. Gold decoration of the chalcopyrite surface to promote SERS allows thin product layers to be observed. Figure 1 shows a chalcopyrite surface oxidised in the transpassive region under N_2 for 1 minute that was subsequently decorated with gold deposited via vacuum evaporation. A S-S stretch band was clearly evident near 454 cm^{-1} , in conjunction with the major chalcopyrite lattice mode near 290 cm^{-1} , and the absence of significant S-S-S bending modes at 220 cm^{-1} (in rhombohedral S_8 I_{470}/I_{220} is approximately 1 – clearly in the surface structure the bending modes are absent and the stretching modes are significantly shifted). No surface product bands were evident prior to gold deposition. In figure 2 a freshly ground chalcopyrite surface was decorated with gold and then cycled in 0.1M HCl under N_2 . The results are consistent with the *ex situ* data, and bear a significant

likeness to published spectra of polymeric sulfur [2]. Potentiodynamic techniques in conjunction with SERS provides important information on initial thin product layers.

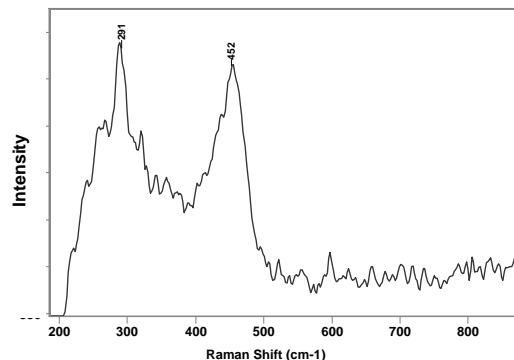


Figure 1 Raman spectra of an enhanced oxidised chalcopyrite surface (100-750 mV/Ag/AgCl, 10 mV/s) with evaporated gold in air (9s accumulation; 10s cycle; excitation source: HeNe (633 nm); Excitation power: 6 mW)

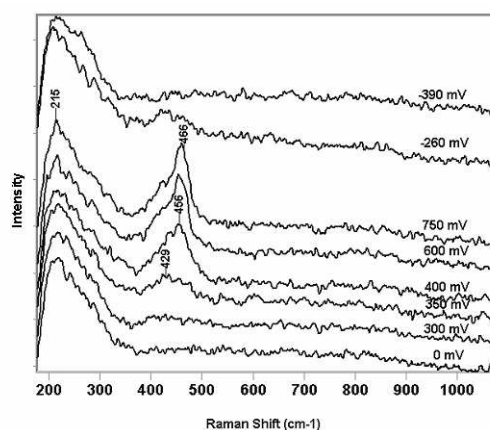


Figure 2: Raman spectra collected from enhanced chalcopyrite surface during cyclic voltammogram (2 mV/s) in 0.1M HCl under N_2 (9s accumulation; 10s cycle; excitation source: HeNe (633 nm); Excitation power: 6 mW)

References:

1. R. P. Hackl, D. B. Dreisinger, E. Peters and J. A. King, *Hydrometallurgy*, **39**, 25 (1995).
2. B. Eckert and R. Steudel, *Topics in Current Chemistry*, **231**, 31 (2003).