

Raman spectroscopic identification of surface species in the leaching of chalcopyrite

Gretel Parker, Gregory A. Hope and Ronald Woods
School of Science Griffith University
Nathan, Queensland 4111, Australia

It is well established that the rate of metal leaching from chalcopyrite [CuFeS₂] under ambient conditions is limited due to the formation of a metal-deficient passivating layer, the composition and formation of which is poorly understood. Cyclic voltammograms in acid solution display an anodic pre-wave during which the passivating film is formed [1]. Raman spectroscopy provides an *in situ* method of identifying surface species, and spatial variations in composition, provided the layer is >5 nm, the detection limit of this technique. The integration of Raman spectroscopy with potentiodynamic techniques provides a powerful tool to assist in understanding complex systems.

A knowledge of the Raman spectra of a range of compounds that are potential products is required in order to identify surface phases. There are a number of stable and metastable phases in the Cu/Fe/S system. To explore the binary Cu/S system, a thin layer of Cu₂S was anodised at different potentials and spectra recorded when the current had decreased to zero. The spectrum from Cu₂S displayed only a broad, low intensity band around 300 cm⁻¹ (Fig.1). The spectrum remained the same as the potential was held at values at which Cu₂S oxidises to Cu_{1.93}S, Cu_{1.83}S and Cu_{1.67}S [2]. At potentials where Cu₄₀S (spionkopite), is formed, a sharp band appeared at 474 cm⁻¹ due to the appearance of S-S pairs. The S-S stretch band was the dominant feature of the spectrum from the surface when the potential was increased into the region in which covellite (CuS) is formed. These results show that Raman spectroscopy can distinguish between copper sulfides with and without S-S bonding, but not between stoichiometries within these two groups. The Raman spectrum, together with the electrode potential can, however, identify the species present. A spectrum from a mineral sample of covellite is shown in Fig. 1.

A number of sulfides exist in the Cu/Fe/S system that contain S-S bonds: pyrite, FeS₂, displays a S-S stretching mode band at 380 cm⁻¹ (Fig.1) which is significantly different from that for covellite. In order to ascertain how the frequency of the S-S stretch band changes when both copper and iron are together in the lattice, a Raman spectrum from idaite (Cu₅FeS₆) was recorded. Fig. 1 shows the spectrum from this mineral compared with those of covellite and pyrite. The S-S band for idaite appears at 466 cm⁻¹. Thus, covellite can be distinguished from other phases in the Cu/Fe/S system that contain S-S bonds, and the position of the S-S stretch vibration provides information on the iron content of the phase.

Elemental sulfur and polysulfides also contain S-S linkages and display sharp S-S stretch bands in Raman spectra at 470 cm⁻¹. This band overlaps with that from covellite when both species are present on the same region of the surface. Thus, covellite cannot be distinguished from sulfur from this band alone. Sulfur also displays an equally strong band from S-S-S chain bending at 215 cm⁻¹ [3] (Fig. 1) which is not found in covellite and the ratio of the intensities of the two bands can potentially be used to distinguish the two phases.

Chalcopyrite, CuFeS₂, is tetragonal with eight atoms in the Bravais space cell and belongs to the D_{2d}¹² space

group. The strongest Raman band at ≈293 cm⁻¹ (Fig. 1) has been assigned to the symmetric anion A₁ mode [4]. It is clear from this figure that the other phases presented can be distinguished from chalcopyrite using Raman spectroscopy.

Figure 2 shows selected spectra from a surface of chalcopyrite from Mt Isa that contained negligible inclusions of other mineral phases. Also presented is a spectrum after the mineral has been immersed for one week in a solution containing 0.03 mol dm⁻³ iron(III) sulfate and 0.1 mol dm⁻³ H₂SO₄ (Eh = 0.865V vs SHE). It can be seen that a covellite-like phase has developed on the mineral surface. Elemental sulfur was also detected in experiments with chalcopyrite samples that contained inclusions of other minerals. Mapping showed that surface product formation was heterogeneous and could be related to initial surface structure and composition of the sample.

References

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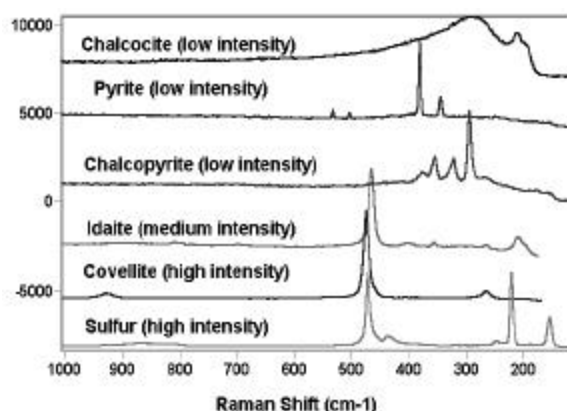


Fig. 1 Raman spectra of a range of minerals in the Cu/Fe/S system

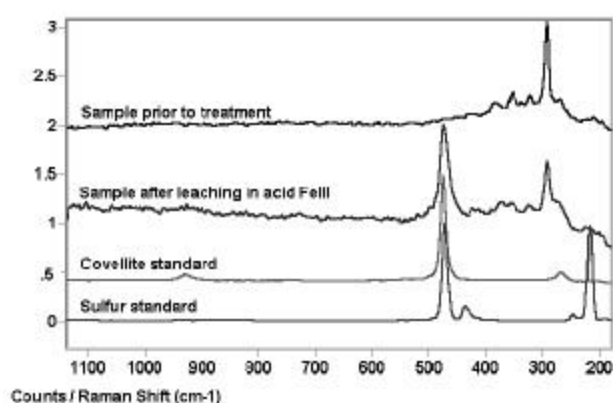


Fig. 2 Selected Raman spectra of chalcopyrite before and after leaching in acidic ferric sulfate solution together with spectra from covellite and sulfur.