



Technical note

## Photocurrents at chalcopyrite and pyrite electrodes under leaching conditions



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### ABSTRACT

The use of photocurrents at transition metal sulfide minerals as a diagnostic tool to assess the relevance of semiconducting properties in the kinetics and mechanisms of dissolution should be applied with caution. It is shown that apparent photocurrents at chalcopyrite and pyrite electrodes at potentials relevant to oxidative dissolution in acidic sulfate solutions are due to thermal and not photocurrent effects when assessed with normal light sources. The use of laser diodes as light sources of variable wavelength has been shown to confirm the thermal effects in both anodic and cathodic reactions involving chalcopyrite and pyrite electrodes. No photocurrents could be detected at either of these minerals except for chalcopyrite under anodic conditions when exposed to radiation from a violet laser diode (405 nm). This observation is attributed to the semiconducting properties of the so-called passivation layer formed on the mineral under anodic polarization and not to the properties of chalcopyrite itself.

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### 1. Introduction

As part of an extensive investigation of the electrochemistry of chalcopyrite as applied to ambient temperature dissolution in concentrated chloride solutions, preliminary tests suggested that apparent photocurrents observed by exposing an electrode surface to radiation from an LED flashlight showed that the relatively small effects on both anodic and cathodic processes could be attributed to thermal effects due to heating of the mineral surfaces. These results will be published in two subsequent papers on the kinetics of the reduction of iron(III) and copper(II) and the oxidation of iron(II) and copper(I) on chalcopyrite in chloride solutions.

In a recent paper (Crundwell et al., 2015), it was shown that photocurrents could be observed at a chalcopyrite electrode when exposed to radiation from a 2 watt LED source at various anodic potentials in dilute sulfuric acid solutions. These results together with apparent correspondence between carrier concentrations determined by Hall effect measurements on the mineral and derived from Mott–Schottky plots at various anodic potentials were used to suggest that the semiconducting properties of chalcopyrite are relevant under oxidative leaching conditions. Furthermore, it was suggested that the so-called passivation in which anodic currents at constant potential in both sulfate and chloride solutions decay with time over extended periods could be interpreted solely on the basis of the semiconducting behavior of chalcopyrite and did not involve inhibition due to the formation of a copper-deficient layer on the surface under these conditions.

In the light of our conclusions mentioned above in chloride system, it was considered important to establish whether the currents observed

by the above authors in sulfate solutions are true photocurrents. In the case of chalcopyrite with a band-gap energy of 0.35 eV (Xu and Schoonen, 2000) that corresponds to radiation of wavelength 3543 nm and pyrite with a band-gap of 0.95 eV (1305 nm), both minerals should respond to radiation throughout the visible region and, for p-type samples, photocurrents should normally be observed using visible sources under anodic but not cathodic conditions (Gerischer, 1966).

### 2. Experimental

Mineral electrodes were prepared from natural samples of high purity that were cut into small cubes of side 3–8 mm. XRD and chemical analysis was used to confirm the purity of the samples. Chalcopyrite samples from Messina and China and pyrite from Australia were used. All samples were established as p-type from the sign of the experimental thermoelectric potential. The samples were fabricated as electrodes using silver epoxy as the contact of one face to a stainless steel stud that was encased in epoxy resin and machined to a cylindrical shape. The electrodes were mounted vertically in a small cell with the mineral face exposed to the solution and the light source as shown in Fig. 1.

Electrochemical measurements were carried out using a standard three-electrode system with working mineral electrodes. Potentials and currents were measured and controlled by a Solartron 1285 potentiostat operated with corrosion measurement software. The silver/silver chloride (3 mol/L potassium chloride) reference electrode (0.207 V versus SHE) was separated by a Luggin capillary from the solution in the cell and the potentials were measured, controlled and

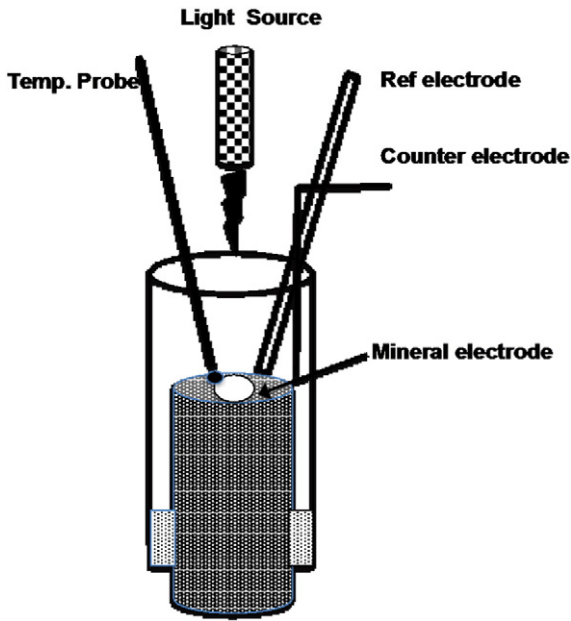


Fig. 1. Experimental setup.

shown relative to this electrode at room temperature. A platinum wire was used as the counter electrode. In a separate experiment a gold disk electrode was used as the working electrode.

In addition to the electrodes, a small temperature probe constructed from a miniature thermistor (bead diameter 0.8 mm) was used to monitor the temperature of the mineral (or gold) electrode surface by locating the bead on the mineral surface. The current through the thermistor at 0.1 V was recorded as a function of time simultaneously as the electrode current and was calibrated using water at various temperatures in the range 20 to 30 °C.

The electrodes were illuminated from above with visible radiation using either a Thrunita TN30 LED flashlight that could be operated at various nominal power levels from 2.5 to 32 W or to one of three laser diodes adapted from laser pointers operated at elevated voltages. The red diode had an operating wavelength of 650 nm, the green 532 nm and the violet 405 nm while the corresponding operating electrical (not optical) power levels were 150, 475 and 450 mW respectively. In addition to the ability to assess the effects of source energy on any photocurrent response, the diodes had the advantage that the laser spot on the surface of the electrodes (1–3 mm in diameter) was small enough such that the thermistor probe could be located outside the excitation area thereby eliminating any possible effects of the radiation on the thermistor response.

The electrolyte contained 0.5 M sulfuric acid and, for the cathodic measurements, 3 g/L iron(III) added as ferric sulfate. Electrochemical measurements were carried out using the following procedure. After polishing and mounting the mineral electrode, approximately 10 cm<sup>3</sup> of electrolyte of the required composition was added to the cell that was not thermostatted as the room temperature was controlled to within 0.5 °C at 24 °C. The electrodes were polished with 3000 grit water paper before each experiment. The rest or open-circuit potential of the mineral electrode was recorded for a period of 5 min after which the potential was stepped to the desired potential and the current recorded as a function of time.

The procedure adopted by the above authors was followed and approximately 200 s after the potential was stepped to the desired value, the appropriate light source was activated for 200 s after which it was de-activated. This could be repeated several times

during the potentiostatic polarization period that was generally 20 to 30 min.

### 3. Results and discussion

In terms of relevance in the oxidative leaching of minerals, it is important to restrict the range of potentials to be studied to within a few hundred millivolts of the mixed potential experienced by the minerals under typical leaching conditions. Thus, in the case of chalcopyrite, the mixed potential in the presence of 3 g/L iron(III) was found to be about 0.45 V while it is 0.48 V for pyrite and therefore the positive limit was set at 0.8 V and the negative at 0.1 V.

The effects of light from the LED flashlight on the current during potentiostatic polarization of the Messina chalcopyrite electrode at 0.577 V and the China electrode at 0.637 V are shown in Fig. 2 for two levels of electrical power. Also shown is the simultaneous recording of the Messina mineral surface temperature. The increase in current on irradiation is similar to the results obtained by Crundwell et al. making allowance for the fact that their system used a rotating electrode that would assist in dissipating the heat generated on the surface by absorption of the incident radiation. On the other hand, the coarser surface (1200 as opposed to 3000 grit in this study) would have increased absorption of the incident radiation. The increased surface temperature is obvious and amounts to about 2 °C at 2.5 W and 5 °C at 8 W. These are probably lower limits as the probe is only in partial physical contact with the mineral surfaces and the complex and different heat transfer processes at the mineral and probe surfaces will result in different temperature–time profiles.

A separate experiment showed no measurable temperature increase when the probe was lifted about 3 mm above the mineral surface when using the LED torch as source.

Assuming an activation energy of 80 kJ/mol for the anodic process (this is reasonable in terms of published data for the effect of temperature on the dissolution of chalcopyrite in sulfate systems (Dutrizac, 1981) and our measurements of the anodic process in the chloride system), one can estimate that an increase of 1 °C in temperature at 25 °C would increase the anodic current by 11%. This increase is consistent with those observed at both electrodes as shown in Fig. 2.

The effect of temperature is further illustrated by the data shown in Fig. 3 for the cathodic reduction of iron(III) on both chalcopyrite and gold electrodes.

The increased (in absolute terms) currents are similar in magnitude to those shown in Fig. 2 and can only be ascribed to temperature effects as a p-type semiconductor should not normally show photocurrents in a cathodic reaction except possibly at very negative potentials and gold, of course, is metallic.

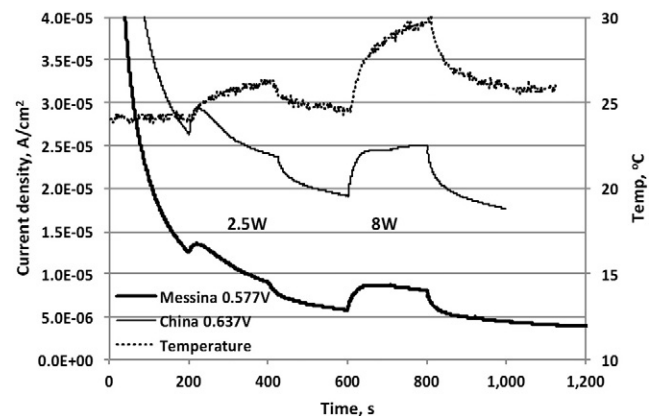


Fig. 2. Response of the anodic current at chalcopyrite electrodes to illumination of light from an LED flashlight while potentiostatted in 0.5 M sulfuric acid at 25 °C. Also shown is the temperature of the surface (Messina) as recorded by the micro-probe.

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