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Accepted Manuscript

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PII: S0304-386X(16)30108-6
DOI: doi: 10.1016/j.hydromet.2016.03.018
Reference: HYDROM 4326

To appear in: Hydrometallurgy

Received date: 15 December 2015
Revised date: 22 March 2016
Accepted date: 27 March 2016

Please cite this article as: Nicol, Michael J., Photocurrents at chalcopyrite and pyrite electrodes under leaching conditions, Hydrometallurgy (2016), doi: 10.1016/j.hydromet.2016.03.018

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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 (405nm). 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.

Keywords: sulfide minerals, electrochemistry, photocurrents, semiconductor

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 behaviour 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 0.35eV (Xu and Schoonen, 2000) that corresponds to radiation of wavelength 3543nm and pyrite with a band-gap of 0.95eV (1305nm), 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 Figure 1.

Figure 1. Experimental setup.
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 (3mol/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 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 0.8mm) 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 0.1V 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 Thrunite TN30 LED flashlight that could be operated at various nominal power levels from 2.5 to 32 watts or to one of three laser diodes adapted from laser pointers operated at elevated voltages. The red diode had an operating wavelength of 650nm, the green 532nm and the violet 405nm 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 0.5M 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$^3$ 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 minutes 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 200s after the potential was stepped to the desired value, the appropriate light source was activated for 200s after which it was de-activated. This could be repeated several times during the potentiostatic polarisation period that was generally 20 to 30 minutes.

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 0.45V while it is 0.48V for pyrite and therefore the positive limit was set at 0.8V and the negative at 0.1V.
The effect of light from the LED flashlight on the current during potentiostatic polarization of the Messina chalcopyrite electrode at 0.577V and the China electrode at 0.637V are shown in Figure 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 2.5W and 5°C at 8W. 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 3mm above the mineral surface when using the LED torch as source.
Figure 2. Response of the anodic current at chalcopyrite electrodes to illumination of light from an LED flashlight while potentiostatted in 0.5M sulfuric acid at 25°C. Also shown is the temperature of the surface (Messina) as recorded by the micro-probe.

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 Figure 2.

The effect of temperature is further illustrated by the data shown in Figure 3 for the cathodic reduction of iron(III) on both chalcopyrite and gold electrodes.
Figure 3. Response of the cathodic current at chalcopyrite and gold electrodes to illumination of light from an LED flashlight while potentiostatted in 0.5M sulfuric acid containing 3 g/L iron(III) at 25°C.

The increased (in absolute terms) currents are similar in magnitude to those shown in Figure 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.

In order to further assess the validity and relevance of photocurrent measurements made using high power light sources, measurements were made using laser diodes that also had the advantage of illuminating only a fraction of the surface of the minerals. The results of such an experiment are shown in Figure 4 for a Messina electrode polarized at 0.646V after an open-circuit period of 300s during which illumination with any of the laser diodes showed no effect on the open-circuit...
potential. At roughly 200s intervals after polarization, the surface was exposed successively to red, green and violet lasers for approximately 50s while the temperature was recorded as before. It is apparent that the red laser (650nm) induced no photocurrents and the relatively low power resulted in only a small temperature increase. The green laser (532nm) increased the measured temperature by about 0.5°C and showed a small apparent photocurrent that could be attributed to surface heating. On the other hand, illumination with the violet laser (405nm) resulted in immediate and very significant (almost 3-fold increase in current) photocurrents that cannot be attributed to surface heating given that the increase in temperature is almost identical to that generated by the green laser.

Figure 4. Response of the anodic current at chalcopyrite to illumination of light from three laser diodes while potentiostatted in 0.5M sulfuric acid solution at 25°C. Also shown are the measured surface temperatures of the electrode.
After approximately 1200s polarization at 0.646V (Figure 4), the electrode was open-circuited and the potential measured as a function of time. The resulting potential decayed slowly as shown by the red curve in Figure 5 and reached about 0.475V after 200s at which point the violet laser was activated and, after a short positive spike in potential, it decayed to about 0.470V after 25s at which point the laser was switched off. The potential remained at this value until the electrode was further potentiostatted at 0.767V and the effect of illumination with violet and green laser diodes monitored as before. Again, the current increased almost 3-fold when the violet laser was used while the very small increase with the green laser was again probably due to surface heating.

Figure 5. Response of the potential (red curve) to illumination of light from the violet laser diode while open-circuit for 300s after the polarization shown in Figure 4. The electrode was subsequently polarized at 0.767V and the effect of illumination by violet and green lasers on the current is shown as the blue curve.
As indicated previously, a p-type semiconductor should not normally exhibit photocurrents for a cathodic process and the results shown in Figure 6 confirm that negligible increases in current were observed for the reduction of iron(III) when illuminated with the three laser diodes.

Figure 6. Response of the cathodic current for the reduction of iron(III) at chalcopyrite to illumination of light from three laser diodes while potentiostatted in 0.5M sulfuric acid solution containing 3 g/L iron(III) at 25°C.

The results of this limited study have shown that apparent photocurrents observed during anodic oxidation of chalcopyrite using light from an LED flashlight can be attributed to heating of the mineral electrode surface. Real photocurrents can only be observed when radiation with a wavelength below 532nm and above 405nm is used and then only during anodic oxidation of chalcopyrite. No photocurrents are observed during cathodic reduction of iron(III). The effect of illumination by the violet laser on
the open-circuit potential is only observed after anodic polarization. These results suggest that chalcopyrite itself does not display semiconducting behaviour expected from a p-type material with a band-gap of 0.35eV in that photocurrents should be observed with any radiation within the visible region. The fact that photocurrents are observed only with light of wavelength 405nm and not 532nm suggests that the surface during anodic oxidation displays semiconducting behaviour that is p-type and that the band-gap is between about 2.3 and 3.1 eV. This conclusion is consistent with the suggestion by Ghahremaninezhad et al (2010) that the so-called passivation layer has semiconducting properties.

An n-type pyrite sample was also subjected to the same experimental procedure and the result shown in Figure 7 for illumination with the violet laser diode.
Figure 7. Response of the anodic current at pyrite to illumination of light from a violet (405nm) laser diode while potentiostatted in 0.5M sulfuric acid solution at 25°C. Also shown are the measured surface temperatures of the electrode.

Unlike chalcopyrite that exhibited anodic photocurrents at 405nm, pyrite shows no only small increases in current that can be attributed to thermal effects. Thus, there is no evidence of semiconducting effects that would have been predicted given the band-gap of 0.95eV. No photocurrents were observed for the reduction of iron(III) on pyrite as in the case of chalcopyrite. The potentiostatic current-time response is also very different to chalcopyrite in that the current rapidly attains a steady-state value for pyrite whereas steady-state is not achieved even after long periods (greater than 12 hours) for chalcopyrite. This suggests that either no anodic passivation occurs on pyrite or that any possible product layer is not semiconducting. Previous publications (Crundwell, 1988 ; Mishra and Osseo-Asare, 1988 ; Bryson and Crundwell, 2014) suggesting that the semiconducting properties of pyrite are important in defining the mechanism of anodic dissolution under oxidative leaching conditions cannot be supported by the evidence in Figure 7.

4. References


Highlights

Apparent photocurrents at chalcopyrite and pyrite electrodes due to thermal effects when assessed with normal light sources.

Laser diodes of variable wavelength confirm the thermal effects in both anodic and cathodic reactions.

No photocurrents at either of these minerals except for chalcopyrite under anodic conditions when exposed to violet laser diode (405nm).

Semiconducting properties due to passivation layer on chalcopyrite