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Anodic Oxidation of Iron(II) and Copper(I) on Various Sulfide Minerals in Chloride Solutions

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Abstract

A comparative study of the electrochemical oxidation of iron(II) and copper(I) ions on selected sulfide minerals in concentrated chloride solutions has been carried out as part of a broader study of the kinetics of the leaching of chalcopyrite, covellite, enargite and pyrite under chloride heap leaching conditions. Mixed potential, cyclic voltammetric and potentiostatic measurements have been made using rotating disk electrodes of massive mineral samples. For comparative purposes, arsenopyrite and platinum electrodes have also been used under the same conditions. The mixed potentials of the various minerals in solutions containing 4 mol/L sodium chloride, 0.1mol/L hydrochloric acid and 0.05 mol/L iron(II) or 0.05 mol/L copper(II) ions at 25°C are all governed by the potentials of the redox couples with the exception of chalcopyrite in solutions of iron(II) for which the mixed potential is lower than the equilibrium potential of the iron(III)/iron(II) couple.

Cyclic voltammetry conducted at potentials positive to the mixed potentials at slow sweep rates has shown variable reactivity of the minerals for oxidation of both iron(II) and copper(I) ions. Oxidation of copper(I) occurs readily on all minerals with the limiting current density observed on all with the exception of chalcopyrite for which the limiting current is not reached even at relatively large overpotentials. Partial passivation of the oxidation of copper(I) is observed at potentials above about 0.7V on covellite. Oxidation of iron(II) is slower than that of copper(I) on all minerals and the limiting
current density is only observed on pyrite. Partial passivation of the oxidation of iron(II) is observed with all other minerals at potentials above 0.65 to 0.75V.

Quantitative measurements of the rates of oxidation at the mixed potentials have been obtained from linear polarization measurements and the results compared with previously published data on the cathodic reduction of iron(III) and copper(II) on these mineral surfaces. The rate constant varies by about an order of magnitude within the mineral group for both iron(II) and copper(I) oxidation and the rates of oxidation on platinum are higher for both couples than for the mineral electrodes. The ratio of the rate of copper(II) reduction to iron(III) reduction is significantly greater for the minerals containing copper than for those without copper.

The effect of illumination with light of wavelength 405nm on the rate of anodic oxidation of iron(II) on chalcopyrite has been evaluated and no positive effects that can be attributed to semi-conducting effects have been observed.

**Keywords:** sulfide minerals, copper(I), iron(II), chloride, oxidation, electrochemistry

1. **Introduction**

The heap leaching of copper ores has become a well-established and important process option for oxide materials and, in recent years, attention has been focused on the leaching of low grade sulfide ores. While this has been largely successful for secondary copper sulfides such as chalcocite and, to some extent, covellite, the slow leaching rates of the primary sulfides such as chalcopyrite and enargite remains an outstanding problem. Recent developments in the application of chloride processes to the heap leaching of chalcopyrite have proved to be promising (Nicol et al, 2011) and this paper is the second of three that will deal with fundamental aspects of the dissolution of chalcopyrite and associated sulfide minerals in relatively concentrated chloride solutions.
It is now generally accepted that the oxidative dissolution of sulfide minerals is electrochemical in nature and can be described by the mixed potential model in which anodic dissolution of the metal sulfide is coupled to cathodic reduction of an oxidant such as iron(III). The problem with chalcopyrite and enargite and, to a lesser extent other sulfide minerals such as covellite and pyrite is the formation of passive or partially passive metal sulfide layers that are formed under anodic oxidation particularly at the low temperatures typical of heap leaching.

More recent unpublished but patented research and development has demonstrated that direct oxidative dissolution of chalcopyrite can be successfully used in column and crib leaching of ores containing primarily chalcopyrite by increasing the chloride concentration in conjunction with other operating modifications. (Patino et al, 2014) Fundamental studies have demonstrated that the mixed potential model applies under these conditions.

A fundamental description of the dissolution of chalcopyrite under these conditions requires knowledge of the mixed potentials, the characteristics of anodic dissolution of the mineral and the cathodic reduction of the oxidants which are both iron(III) and copper(II) in chloride solutions. The anodic oxidation of the reduced forms of the oxidants is also of indirect importance as this information is required for a full description of the mixed-potential model (Nicol, 1993). In addition, the anodic reactions can be used as possible probes for the formation of “passive” layers on the sulfide minerals. A previous paper (Nicol et al, 2016) has dealt with the cathodic reactions of these oxidants and a later paper will deal with the anodic characteristics of the minerals in concentrated chloride solutions. The presence of other sulfides such as covellite, enargite and pyrite in such ores requires that the study also include, in a more superficial way, the electrochemical behavior of these minerals under identical conditions.
Arsenopyrite has been included to provide an additional sulfide that does not contain copper while platinum has also been added to the list as a comparative inert substrate for the anodic reactions.

2. Experimental

Details of the mineral samples used and the electrochemical methods and experimental procedures have been provided in a previous publication (Nicol et al, 2016). As previously described, electrochemical measurements were carried out using a standard three-electrode system with working mineral electrodes rotated at 500 rpm.

The base electrolyte contained 4M sodium chloride and 0.1M hydrochloric acid. Solutions were prepared using ferrous chloride and cuprous chloride (Ajax Chemical), analysed by potentiometric titration with standard chromium(VI) solution and kept under nitrogen. Due to the presence of small amounts of iron(III) and copper(II) in the reagents and unavoidable oxidation during preparation and measurement (conducted using solutions sparged with high-purity nitrogen), the solutions contained variable amounts of the oxidised ions. The potential of a platinum electrode was used to establish that the concentrations of the oxidised metal ions was less than 5% of the reduced forms.

A silver/silver chloride (3mol/L potassium chloride) reference electrode (0.207 V versus SHE) was used and the potentials were measured and controlled relative to this electrode at room temperature (25±0.5°C). All potentials are shown relative to the standard hydrogen electrode (SHE).

In the case of the cyclic voltammetry (at a low sweep rate of 0.2mV/s), the potentials were manually corrected for the voltage drop in each sample electrode using the resistance values as measured in the determination of the mineral resistivity. These corrections were made automatically during the potentiostatic experiments.
Photocurrent measurements on chalcopyrite in solutions containing iron(II) were made as previously described. (Nicol, 2016)

3. Results and discussion

3.1. Mixed potential measurements

With the exception of chalcopyrite in solutions containing iron(III), the measured mixed potentials after immersion for 5 minutes were all within 5mV of the potential as measured by a platinum electrode. This confirms that the mixed potential is determined by the equilibrium potential of the relevant redox couple and that the rate of anodic oxidation of the minerals is negligible at these potentials in comparison to the rates of oxidation/reduction of the iron(II)/(III) and copper(I)/(II) couples i.e. a so-called Type III system (Nicol, 1993). In the case of chalcopyrite in iron(II) solutions, the rate of oxidation of iron(II) is very slow (see below) and, in this case, the rate of oxidation of the mineral is comparable with a resulting negative shift in the mixed potential.

3.2. Linear sweep voltammetric measurements

The results of the anodic oxidation of iron(II) and copper(I) on each of the minerals are shown for comparison in Figures 1 and 2 as linear sweep voltammograms (plotted on a log scale to accommodate the wide variation) obtained in a positive sweep direction from the mixed potentials. For all minerals with the exception of chalcopyrite, anodic currents at potentials in the region of interest in the absence of iron(III) or copper(II) were found to be small as will be shown below. Thus, the currents shown in Figures 1 and 2 can be attributed to the oxidation of iron(II) and copper(I) respectively.
Figure 1. Linear sweep voltammograms for the minerals in base electrolyte containing 0.05M iron(II).

Examination of the curves shows that there are significant differences in reactivity for the oxidation of iron(II) with only the rate on pyrite exhibiting relatively reversible behaviour similar to platinum. In the case of the other minerals, the maximum current

Figure 2. Linear sweep voltammograms for the minerals in base electrolyte containing 0.05M copper(I).
densities are lower and most curves pass through a maximum at potentials between about 0.65 and 0.75V. The differences are not so marked in the case of the oxidation of copper(I) ions and only covellite provides evidence of partial passivation at potentials above about 0.75V. In this context, the term “passivation” will be used to describe a reduction in the rate of an anodic process that occurs as the potential increases. Depending on the rate at which the process responsible for passivation occurs, this reduction in rate can appear as a relatively small peak or shoulder on a voltammogram but can be observed as significant decays in current in potentiostatic measurements over longer times.

The limiting current density for mass transport controlled oxidation of 0.05M iron(II) can be calculated from the Levich equation to be 119 A/m$^2$ and 150A/m2 for the oxidation of copper(I) at 500rpm. These estimates were made using data for the diffusion coefficients obtained previously (Nicol et al, 2016). Thus, the limiting current density is only approached at high potentials for the oxidation of iron(III) in the case of pyrite (and platinum) while limiting current oxidation of copper(I) is achieved on all minerals. The slightly lower limiting current in the case of pyrite is due to a lower copper(I) concentration in this case while the limiting current is approached more slowly in the case of chalcopyrite.

Details of the behaviour of each mineral will be discussed in the following section.

Comparative results for the oxidation of iron(III) and copper(I) are shown in Figure 3 for pyrite which also includes the voltammogram obtained in the base electrolyte in the absence of iron(II) or copper(I) ions.
Figure 3. Linear sweep voltammograms for the oxidation of iron(II) and copper(I) on pyrite. Also shown is the voltammogram for the oxidation of the mineral in the absence of iron(II) and copper(I) (right hand ordinate).

The reverse sweeps have been omitted from the voltammograms obtained in the presence of iron(II) or copper(I) as the hysteresis between the forward and return sweeps is small. In the case of pyrite, the greater reactivity for oxidation of copper(I) than iron(II) is apparent from the slopes of the curves although, at high potentials, both processes become mass transport controlled. There is no evidence of passivation due to changes in the mineral surface in this potential range i.e pyrite is well-behaved in this respect.

For arsenopyrite as shown in Figure 4, hysteresis is observed in the reverse sweeps indicating the anodic formation of inhibiting surface layer(s) for the oxidation of both copper(I) and iron(II). The maximum current density for oxidation of copper(I) at the peak around 0.7V is some thirty times the maximum for the oxidation of iron(II). Although not obvious in Figure 4, the sweep in the absence of iron(II) and copper(I) shows no evidence of a peak in this potential region.
Figure 4. Linear sweep voltammograms for the oxidation of iron(II) (left ordinate) and copper(I) (right ordinate) on arsenopyrite. Also shown is the voltammogram for the oxidation of the mineral in the absence of iron(II) and copper(I) (left ordinate).

In the case of chalcopyrite (Figure 5), oxidation of copper(I) proceeds without any apparent passivation (no hysteresis – not shown) and approaches the limiting current density at about 0.7V. Oxidation of iron(II) proceeds at a much lower rate (the maximum current at 0.7V is some 100-fold lower than that for the oxidation of copper(I)). A peak at about 0.7V occurs at the same potential as that observed as a shallow peak in the same region in the absence of copper(I) and iron(II). Thus oxidation of iron appears to be subject to the same passivation process observed during anodic oxidation of the mineral.
Figure 5. Linear sweep voltammograms for the oxidation of iron(II) (left ordinate) and copper(I) (right ordinate) on chalcopyrite. Also shown is the voltammogram for the oxidation of the mineral in the absence of iron(II) and copper(I) (left ordinate).

Similar results were obtained for covellite as shown in Figure 6. In this case the oxidation of both iron(II) and copper(I) are passivated at potentials between 0.65 and 0.7V with the latter showing a broad peak on the forward sweep and partial re-activation during the reverse sweep. Both processes appear to be passivated at the same potential at which anodic oxidation of the mineral shows passivation with the shape of the curve for the oxidation of iron(II) closely following that of the mineral itself. The peak current density for the oxidation of copper(I) is some 240 times that for the oxidation of iron(II).
Figure 6. Linear sweep voltammograms for the oxidation of iron(II) (left ordinate) and copper(I) (right ordinate) on covellite. Also shown is the voltammogram for the oxidation of the mineral in the absence of iron(II) and copper(I) (left ordinate).

A similar peak current density at a potential of 0.68V is observed during the oxidation of iron(II) on enargite as shown in Figure 7. This peak corresponds to a broad peak in the region of 0.7 to 0.75V for the anodic oxidation of the mineral.

Figure 7. Linear sweep voltammograms for the oxidation of iron(II) (left ordinate) and copper(I) (right ordinate) on enargite. Also shown is the voltammogram for the oxidation of the mineral in the absence of iron(II) and copper(I) (left ordinate).
Like chalcopyrite, oxidation of copper(I) is not affected by oxidation of the mineral and the limiting current density is attained at about 0.75V which is some 25 times the peak current density for the oxidation of iron(II).

For comparison, the curves obtained with platinum are shown in Figure 8.

Figure 8. Linear sweep voltammograms for the oxidation of iron(II) and copper(I) on a platinum electrode.

The large difference in the reactivity for the oxidation of copper(I) and iron(II) was unexpected with the limiting current density for the oxidation of the latter not attained even at a potential of 0.85V.

3.3. Linear polarization measurements

Although not shown in the voltammograms in Figures 3 to 8, the voltammetric sweeps were initiated some 50mV negative to the rest potentials and therefore a small cathodic section was recorded before the anodic section shown. This allowed for the measurement of the slope of the curves at the mixed (in this case close to the equilibrium potentials for the relevant copules) potential by plotting the current density at various potentials 5mV on either side of the mixed potentials. In each case, the plot of
current density was a linear function of the potential over this range and, as an example, the plots for chalcopyrite are shown in Figure 9.

**Figure 9.** Linear polarization plots for the iron(III)/(II) and copper(II)/(I) couples on chalcopyrite.

This linear polarization technique (Oldam and Myland, 1994) can be used to derive kinetic information. Thus, as outlined in the Appendix, the electrochemical rate constants (k) for the copper(I)/(II) and iron(II)/(III) couples can be derived from the slopes of these plots and the values obtained are summarized in Table 1. The rate constants shown for comparison in parentheses in Table 1 are those obtained by fitting the cathodic reduction curves for iron(III) and copper(II) to a modified version of the Butler-Volmer equation as obtained in separate experiments as described in a previous publication. (Nicol et al, 2016). The method described in this previous publication could not be generally used to derive kinetic information in this case because of the passivation processes that occur at potentials positive to the rest potentials for many of the minerals does not permit the use of the Butler-Volmer equation.
Table 1. Electrochemical rate constants at 25°C

<table>
<thead>
<tr>
<th>Sulfide</th>
<th>Semiconductor type</th>
<th>$10^7 \times k$ Cu(II)/(I) m/s</th>
<th>$10^7 \times k$ Fe(III)/(II) m/s</th>
<th>$k_{Cu}/k_{Fe}$ Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS$_2$</td>
<td>n</td>
<td>64(60)</td>
<td>14.3(5.5)</td>
<td>8</td>
</tr>
<tr>
<td>FeAsS</td>
<td>p</td>
<td>22(5.5)</td>
<td>3.6(0.75)</td>
<td>7</td>
</tr>
<tr>
<td>CuFeS$_2$</td>
<td>n</td>
<td>20(30)</td>
<td>1.5(0.32)</td>
<td>54</td>
</tr>
<tr>
<td>CuS</td>
<td>-</td>
<td>113(42)</td>
<td>2.3(0.52)</td>
<td>65</td>
</tr>
<tr>
<td>Cu$_3$AsS$_4$</td>
<td>p</td>
<td>26(7.8)</td>
<td>9.3(0.18)</td>
<td>23</td>
</tr>
<tr>
<td>Pt</td>
<td>-</td>
<td>&gt;150(&gt;500)</td>
<td>&gt;25(&gt;500)</td>
<td>-</td>
</tr>
</tbody>
</table>

With the exception of the data for the copper(II)/copper(I) couple on chalcopyrite, all rate constants derived from the anodic results obtained for the oxidation of copper(I) and iron(II) are greater than those derived from the cathodic results. This consistent difference illustrates that the surfaces of these minerals generally exhibit reduced electrocatalytic properties at the higher potentials from which cathodic reduction of iron(III) and copper(II) were studied. Thus the rate constants derived from the kinetics of the cathodic reactions were obtained at potentials in the range 0.65 to 0.75V whereas those derived (in the present study) from the kinetics of the anodic reactions were obtained at potentials between 0.54 and 0.60V. It is tempting to relate this observation with the appearance of peaks or shoulders at potentials above about 0.6V during anodic oxidation of the minerals in the absence of copper(I) or iron(II) ions. The opposite trend is observed with platinum in that its surface appears to be more catalytic at the higher potentials.

As pointed out in the previous publication, the relative rates of electron transfer to the copper(II)/couple(I) are greater than that for the iron(III)/iron(II) couple for all minerals (including platinum) and that the ratio is greatest for the minerals containing copper.
This has obvious practical implications in the optimization of the rates of heap leaching of these minerals in chloride solutions.

3.4. Potentiostatic measurements

In order to establish longer term behaviour during oxidation of iron(II) and copper(I), potentiostatic measurements were made in which the potential was held at various potentials and the current monitored as a function of time. The potentials selected for each mineral were aimed at values below and above those identified in the voltammograms as indicating passivation of the anodic reactions.

The results obtained with pyrite as shown in Figure 10 confirm the absence of hysteresis in the voltammetry in that steady currents are obtained within seconds of application of the potential for the oxidation of both iron(II) and copper(I). The rate of oxidation of the latter is mass transport controlled at 0.745V whereas the oxidation of iron(II) is below the limiting value even at 0.800V.

![Figure 10. Potentiostatic transients for the oxidation of iron(II) and copper(I) on pyrite at the potentials shown.](image)

Oxidation of copper(I) on arsenopyrite (Figure 11b) results in stable currents that are rapidly established at both selected potentials with the limiting current density observed
at the higher potential. There does not appear to be evidence of passivation within the 10 minutes studied. However, as indicated by the negative hysteresis in the voltammogram for the oxidation of iron(II) in Figure 4, passivation of the oxidation of this ion is apparent from the falling current transients at all potentials unlike the behaviour of pyrite.

![Graph](b.png)

Figure 11. Potentiostatic transients for the oxidation of (a) iron(II) and (b) copper(I) on arsenopyrite at the potentials shown.

The transients obtained using chalcopyrite are shown in Figure 12.
Figure 12. Potentiostatic transients for the oxidation of (a) iron(II) and (b) copper(I) on chalcopyrite at the potentials shown.

In this case, oxidation of copper(I) occurs uninhibited at 0.591V while there is evidence of slow passivation at the higher potential of 0.740V with the current density declining somewhat from an initial mass-controlled value. The rate of oxidation of iron(II) is low relative to that of copper(I) and decreases rapidly with time at all potentials studied. The results for enargite as shown in Figure 13 reveal that the oxidation of iron(II) undergoes slow inhibition at low potentials (0.627 and 0.664V) but more obvious
passivation at the higher potentials of 0.776V and 0.814V. Oxidation of copper(I) appears to occur without inhibition at both low and high potentials.

![Potentiostatic transients for the oxidation of (a) iron(II) and (b) copper(I) on enargite at the potentials shown.](image)

Figure 13. Potentiostatic transients for the oxidation of (a) iron(II) and (b) copper(I) on enargite at the potentials shown.

The results obtained using covellite are shown in Figure 14. In the case of this mineral, the current for oxidation of copper(I) at a potential of 0.592V is constant over the measurement period while, at the higher potential (above that of the peak in Figure 6)
the current slowly decays to values below that obtained at the lower potential. This is in accord with the peak at 0.65V in Figure 6.

![Graph](image1.png)

(a)

![Graph](image2.png)

(b)

Figure 14. Potentiostatic transients for the oxidation of (a) iron(II) and (b) copper(I) on covellite at the potentials shown.

The rate of oxidation of iron(II) at a potential (0.628V) just below that of the peak also decays slowly while the rate of passivation is greater at the higher potentials.

For all minerals, the rate of oxidation of iron(II) is slower than that of copper(I) which confirms the results obtained in the previous study of the reduction of iron(III) and
copper(II) (Nicol et al, 2016). Passivation of the oxidation of iron(II) at high potentials occurs on all minerals with the exception of pyrite. Slow passivation of the oxidation of copper(I) occurs at high potentials only on chalcopyrite and covellite. In each case, passivation of the anodic reactions can be correlated with the presence of an anodic peak or shoulder at similar potentials observed during oxidation of the relevant mineral in the absence of copper or iron in the solution. Thus, while conclusive evidence to identify the species responsible for passivation of the oxidation of the minerals is yet to be established, it appears that the same species is responsible for passivation of the oxidation of iron(II) and copper(I). These results highlight the value of the study of the kinetics of such redox couples as a means of more definitively establishing the occurrence of passivating layers on the surfaces of such minerals. This will be explored in more detail in the case of chalcopyrite in a subsequent publication.

3.5. Relationship to semiconducting properties.

As shown in recent publications (Nicol, 2016: Nicol et al, 2016), the influence of the semi-conducting properties of the minerals on their behaviour during oxidative dissolution in chloride solutions appears to be minimal. In particular, measurement of photocurrents under anodic and cathodic polarization showed that only chalcopyrite responded to illumination and then only with light having a wavelength of 405nm. Therefore, the effect of such illumination on the anodic currents during the oxidation of iron(II) on chalcopyrite was investigated using the method described in the above publications. The results are shown in Figure 15. In this case, the chalcopyrite electrode was periodically illuminated by a violet diode laser during a positive-going potential sweep in a solution containing both iron(III) and iron(II). Simultaneous measurement of the electrode surface temperature was also made with a thermistor probe.
The small positive deviations in the anodic current density (and negative deviations barely discernable during the cathodic branch) at potentials below about 0.75V during illumination by the laser are accompanied by an increase in temperature of the mineral surface of at least 0.5°C. This increase in temperature can account for the increased (in absolute terms) currents in this region as previously determined (Nicol, 2016).

At potentials above about 0.75V, the deviations are larger and can be correlated with those observed on chalcopyrite in the absence of iron(II) (Nicol, 2016). It appears therefore that the oxidation of iron(II) on chalcopyrite is not influenced by illumination under these conditions. Although photocurrents would not be expected to be observed for a cathodic reaction involving an n-type semiconductor such as this sample of chalcopyrite, they could be expected for an anodic reaction (Gerischer, 1966).

Examination of the data in Table 1 shows that there does not appear to be any correlation between the semiconducting type and reactivity for oxidation of copper(I)
and iron(II). Thus, in terms of the theory of semiconductor electrochemistry, one could
expect to the rates of anodic reactions to be retarded on an n-type material and, although
this is true of the oxidation of iron(II) on chalcopyrite, it is certainly not true of the
anodic oxidation of copper(I) despite the potentials being similar for both the oxidation
of iron(II) and copper(I). The relatively high reactivity of pyrite for the oxidation of
both metal ions is also not expected on this basis. This conclusion supports that of
several previous studies that showed no correlation between the semiconducting
properties of some of these minerals and both electrochemical reactivity (anodic and
cathodic examples) and leach kinetics (Biegler, 1976; Klein and Shuey, 1978; Biegler

4. Conclusions
A comparative study of the electrochemical oxidation of iron(II) and copper(I) ions on
selected sulfide mineral and platinum rotating disk electrodes in concentrated chloride
solutions has been carried out.
The mixed potentials of the various minerals in solutions containing 4 mol/L sodium
chloride, 0.1mol/L hydrochloric acid and 0.05 mol/L iron(II) or 0.05 mol/L copper(I)
ions at 25°C vary little with time and are close to the equilibrium potentials of the metal
ion redox couples as could be expected given the low rates of mineral oxidation at these
potentials
Cyclic voltammetry conducted at potentials positive to the mixed potentials at slow
sweep rates after the mixed potential measurements has shown variable reactivity of the
minerals for oxidation of iron(II) and copper(I) ions. Except for pyrite, all minerals
exhibited at least partial passivation for the oxidation of iron(II) while the oxidation of
copper(I) also showed passivation on chalcopyrite and covellite. Passivation appears to
occur at potentials similar to that observed for the anodic oxidation of the minerals in the absence of iron(II) or copper(I) ions.

The electrochemical rate constants derived from linear polarization measurements shows that all the minerals have greater reactivity for the oxidation of copper(I) than iron(II) ions. The rate constants vary by over an order of magnitude within the mineral group for both iron(II) and copper(I) oxidation and the rates of oxidation on platinum are higher for both couples than for the mineral electrodes.

An attempt has been made to correlate the kinetic data with published data on the semi-conducting properties of the metal sulfides. There does not appear to be any correlation between the semiconducting type of the mineral and the reactivity for electron transfer to the metal ion couples. In addition, small increases in anodic currents for the oxidation of iron(II) during illumination of a chalcopyrite electrode can be accounted for in terms of thermal and not photocurrent effects.

5. Appendix
As outlined in a previous publication (Nicol et al, 2016), the anodic reactions that both involve single electron transfers can be written in the general form

\[ \text{Red} = \text{Ox} + e \]  

The kinetics are best described by the Butler-Volmer equation which is conveniently written in the form

\[ i = kF [\text{Red}] \exp\{(1-\alpha)F(E - E_0)/RT\} - [\text{Ox}] \exp\{-\alpha F(E - E_0)/RT\} \]  

in which,

\[ i \] is the net anodic current density (A/cm²),
\[ F \] is the Faraday (96480 A.s/mol),
\[ k \] is a potential independent electrochemical rate constant (cm/s),
[Ox], is the concentration of the oxidised species at the electrode surface (mol/cm$^3$),

[Red], is the concentration of the reduced species at the electrode surface (mol/cm$^3$)

$\alpha$ is the so-called transfer coefficient (assumed to be 0.5 for simple one-electron transfers),

E is the potential with respect to any reference electrode, V

$E_f$ is the formal (or conditional) potential (V) for the particular solution under study defined as the equilibrium potential at [Ox] = [Red] using the same reference electrode.

The surface concentrations of the reacting species will generally not be equal to the bulk concentrations because of generation or consumption by the electrochemical reactions. However, at potentials close to the equilibrium potential in well agitated systems, the current densities are sufficiently low that one can assume that the surface concentrations are equal to the bulk values [Ox]$_o$ and [Red]$_o$.

Writing $(E - E_f) = (E - E_e) - (E_f - E_e)$ in which $E_e$ is the equilibrium potential under the experimental conditions and substituting in (2) together with the Nernst equation one obtains

$$i = kF [\text{Red}]_o^\alpha [\text{Ox}]_o^{1-\alpha} \exp\{((1-\alpha)f(E)) - \exp\{-\alpha f(E)\}\}$$

in which $f(E) = F(E - E_e)/RT$

For $f(E) \ll 1$, i.e. $E - E_e \ll 0.0591$V at 25°C, one can make the approximation $\exp(f(E)) \sim 1 + f(E)$. Substitution in (3) and rearrangement gives

$$i = kFf(E).[\text{Red}]_o^\alpha [\text{Ox}]_o^{1-\alpha}$$

$$= kF^2/RT. \ [\text{Red}]_o^\alpha [\text{Ox}]_o^{1-\alpha} (E - E_e)$$

Thus, a plot of $i$ versus $(E - E_e)$ is linear from the slope of which $k$ can be obtained assuming $\alpha = 0.5$. 
6. References


**Highlights**

Comparative study of the electrochemical oxidation of iron(II) and copper(I) ions on chalcopyrite, covellite, enargite, pyrite and arsenopyrite in concentrated sodium chloride solutions.

All the minerals have greater reactivity for the oxidation of copper(I) than iron(II).

The rate constant varies by about an order of magnitude within the mineral group for both iron(II) and copper(I) oxidation.

The ratio of the rate of copper(I) oxidation to iron(II) oxidation is significantly greater for the minerals containing copper than for those without copper.

Passivation for the oxidation of iron(II) observed on all minerals except pyrite.

Passivation occurs at potentials similar to those observed for passivation of the anodic oxidation of the minerals.

There do not appear to be any semiconducting effects on the rate of oxidation of iron(II) on chalcopyrite.