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The electrochemistry and kinetics of the oxidative dissolution of chalcopyrite in ammoniacal solutions. Part I – Anodic Reactions

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Abstract

The oxidative dissolution of chalcopyrite in aqueous solutions is an electrochemical process. Such processes can be evaluated as coupled anodic and cathodic reactions using electrochemical techniques. The chalcopyrite dissolution reaction has been studied in ammonia-ammonium sulphate solutions using potentiostatic and potentiodynamic methods. Anodic current densities in the vicinity of the mixed potential have been found to increase with an increase in total ammonia (NH₃+NH₄⁺) from 1 M to 3 M, and the order of reaction was found to be 1st order with respect to ammonia. The reaction was found to be zero order with respect to [OH⁻] at a pH between 9 and pH 10. An analysis of the Tafel slopes suggested an average charge transfer coefficient of 0.61. The rate controlling step was concluded to be a single electron transfer reaction, which supports the formation of a copper depleted intermediate surface that is rapidly oxidised in subsequent electron transfer reactions. The anodic sweeps and constant potential tests did not support the formation of a passivating surface deposit on the oxidising chalcopyrite surface.

Introduction

Ammoniacal leaching has been used for the recovery of non-ferrous metals such as copper, cobalt and nickel from oxide ores. The ammonia based chemistry allows for the selective dissolution of the desired metals leaving behind gangue including iron. Although acid systems especially in the sulphate and chloride systems are the most widely studied and have been reviewed by Walting (2013, 2014), the sulphate system is characterised by slow leach kinetics and passivation of the mineral surface while on the other hand, the cupric-chloride systems offers better kinetics but faces criticism due to the corrosive nature of chloride and the need for fine grinding (Walting, 2014). Ammonia has become more attractive as a lixiviant during the present socio-economic climate due to its low toxicity, relatively low cost and ease of regeneration by evaporation (Meng and Han,
Various commercial hydrometallurgical processes have been developed for the treatment of mineral ores, these include the Sherrit Gordon process which treats sulphide concentrates of nickel, cobalt and copper at temperatures of 95-105 °C and air pressure of 800 - 1000 KPa in the 1950s (Forward and Mackiw, 1955); the Arbiter process (Arbiter and Kling, 1974) for recovering copper from chalcopyrite concentrates at 75 - 80 °C in the presence of oxygen at 34.5 – 55.2 Kpa in the 1970s; and the Escondida process which was intended to produce high grade copper concentrates in the 1990s (Duyvesteyn and Sabacky, 1993).

The oxidative dissolution of sulphide minerals has long been established to be an electrochemical process (Peters, 1976; Crundwell, 1988). This means that the dissolution reaction involves the transfer of electrons between an oxidising and reducing species. Oxidative leaching reactions, such as that of chalcopyrite in the current study, involve the loss of electrons by the mineral which constitutes the anodic reaction and the simultaneous gain of electrons by the oxidising species being reduced, which constitutes the cathodic reaction.

Beckstead and Miller (1977a) studied the ammoniacal leaching of chalcopyrite and reported the leaching reaction to proceed according to Equation (1).

$$2\text{CuFeS}_2 + 8\text{NH}_3 +8.5\text{O}_2 + 4\text{OH}^- = 2\text{Cu}^{2+}\text{(NH}_3\text{)}_4 +2\text{Fe}_2\text{O}_3 + 4\text{SO}_4^{2-} + 2\text{H}_2\text{O}$$  (1)

According to (1), the sulphur in the mineral lattice is oxidised from an oxidation state of -2 to +6, meaning the reaction requires transfer of 8 electrons per sulphur. These 8 electrons would be taken up by the oxygen molecules, and since chalcopyrite has two sulphur atoms, 16 electrons need to be transferred to an oxidant per mole of chalcopyrite oxidised. The remaining 2 electrons transferred in Equation 1 result from the oxidation of Fe(II) to Fe(III).

The oxidative dissolution reaction (1), suggests that the oxidant in this reaction is oxygen as was generally accepted by previous researchers over the years (Forward and Mackiw, 1955; Kuhn, Arbiter and Kling, 1974; Beckstead and Miller, 1977b; Reilly and Scott, 1977; Warren and Wadsworth, 1984; Duyvesteyn and Sabacky, 1993; Arbiter and McNulty, 1999). However, earlier work by the authors (Moyo et al., 2015) showed that copper(II) is the primary oxidant in the system, itself being reduced to copper(I), which would in turn be oxidised back to copper(II) in solution by oxygen. The authors found the number of electrons transferred in the anodic reaction, to be similar in the presence and absence of oxygen, with average values of 7.5 and 7.3 electrons (per CuFeS$_2$), respectively. The authors went on to infer that thiosulphate, is the probable product of oxidation of sulphide and that either copper(I) or copper(II) are the primary products of anodic oxidation at the
potentials studied. In consequence, Moyo et al. (2015) proposed a combination of (2) and (3) to be the anodic reactions.

\[
\text{CuFeS}_2 + 4\text{NH}_3 + 6\text{OH}^- = \text{Cu(NH}_3)_2^{2+} + \text{Fe(NH}_3)_2^{2+} + \text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O} + 7\text{e} \quad (2)
\]

\[
\text{CuFeS}_2 + 6\text{NH}_3 + 6\text{OH}^- = \text{Cu(NH}_3)_4^{2+} + \text{Fe(NH}_3)_2^{2+} + \text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O} + 8\text{e} \quad (3)
\]

The formation of copper(I) as an oxidation product is possible due to its stabilisation in solution by ammonia forming a cuprous ammine complex \( \text{Cu(NH}_3)_2^{+} \) (stability constant \( \log \beta = 10.62 \) in ammonium sulphate solutions at 25 °C (Stupko et al, 1998)). The effect of ammonia on the anodic reaction was evaluated by Warren and Wadsworth (1984), who observed anodic currents to increase with an increase in free ammonia in the concentration range 0.028 to 0.468 M with the pH fixed at 9.2. At relatively higher free ammonia concentrations of 1 M to 4.32 M at pH 10.24, these authors report no dependence on free ammonia at high potentials but they do not mention the apparent lower anodic currents observed at 1 M free ammonia at all potentials. The study by Warren and Wadsworth (1984) was the only one that investigated the effect of ammonia on the anodic reaction, whereas all other papers report on the influence of ammonia on the kinetics of the overall leaching reaction.

While copper(II) had not previously been identified as the oxidant on the chalcopyrite surface, previous investigations (Forward and Mackiw, 1955; Kuhn, Arbiter and and Kling, 1974; Beckstead and Miller, 1977b; Warren and Wadsworth, 1984; Duyvesteyn and Sabacky, 1993; Tozawa, Umestu and Sato, 1976) have reported on its catalytic effects on the overall leaching reaction and on the anodic reaction. Warren and Wadsworth (1984) and Moyo et al. (2015) reported increased rest potentials and increased anodic currents when copper(II) concentrations were increased in solution. However, the effect of copper(II) on cathodic currents on chalcopyrite surfaces has not previously been reported. Although commonly accepted to be the primary oxidant, the effect of direct oxygen reduction on the mineral surface has never been evaluated in the context of ammoniacal chalcopyrite dissolution, but has only been shown to result in increased leaching rates in the course of leaching experiments (Forward and Mackiw, 1955; Kuhn, Beckstead and Miller, 1977b; Reilly and Scott, 1977; Warren and Wadsworth, 1984).

This paper (Part I) is focussed on further characterisation of the anodic reactions (2) and (3), while Part II reports on the cathodic reactions.

**Experimental**

**Chalcopyrite sample**
Samples of natural chalcopyrite from Durango, Mexico (supplied by Ward’s Natural Science, Rochester, NY, USA) were mounted on brass stubs with conductive silver epoxy and the assembly then imbedded in non-conductive epoxy resin. The purity of the bulk sample was confirmed through XRD (results presented in Moyo et al. (2015)), XRF and QEMSCAN analysis. Results from a chemical analysis of the sample using acid digestion followed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and sulphur analysis by LECO indicated 32.0 (mass) % Cu, 30.5% Fe, 33.4% S, 2.4% Zn, and 1.2% Ca. QEMSCAN analysis of the sample indicated it to be 95% chalcopyrite, with small amounts of sphalerite, calcite and quartz (Table 1). XRF indicated the presence of 0.2% silica, 1% zinc and 0.7% lead in the sample. Thus, the sample was accepted as being of high purity. The electrode was inspected under a microscope and analysed using SEM with small fractions of quartz inclusions being identified on the surface. The electrode surface was subjected to a series of polishing stages on SiC abrasive paper of 1200 grit size, then on 1 μm, 0.3 μm and 0.05 μm aluminium oxide prior to each experiment, except where stated. Two electrodes cut from the same chalcopyrite sample were used throughout the course of the study and the exposed surface areas were measured to be 0.428 cm² and 0.360 cm², respectively, using imagej® for image analysis of photographs of the electrode surface.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>% Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>95.24</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>3.32</td>
</tr>
<tr>
<td>Calcite</td>
<td>1.30</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0.11</td>
</tr>
<tr>
<td>Others sulphides</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Test solutions

Test solutions were prepared from deionised water and analytical grade CuSO₄.5H₂O (Merck), NH₄OH (25%, Merk), (NH₄)₂SO₄ (Merk), H₂SO₄ (Merk) and NaOH (Merk). The solution was made by mixing NH₄OH with (NH₄)₂SO₄ at a 1:1 molar ratio of N. e.g. 1 M NH₄OH : 0.5 M (NH₄)₂SO₄. Ammonia concentrations are reported based on total uncomplexed ammonia i.e. (NH₃+NH₄⁺). In experiments requiring the addition of copper at the start of the experiment, the copper was added by dissolving CuSO₄.5H₂O in the ammonia-ammonium sulphate solutions. The ammonia consumed by complexation with added copper (II) was replaced by the addition of stoichiometric amounts of ammonium hydroxide. It was determined that for copper(II)-ammine solutions, the dominant species is the tetra-ammine copper(II) using HSC Chemistry adapted for copper(I) and copper(II)
speciation for copper ammonia systems. In a similar fashion it was determined that for solutions containing copper(I)-ammine, the copper(I) di-ammine is the predominant species under all conditions in the present study. The pH was adjusted by addition of either H₂SO₄ or NaOH solutions.

**Electrochemical measurements**

A standard three-electrode cell with a chalcopyrite rotating disk working electrode was used for all electrochemical measurements. A saturated calomel reference electrode and platinum wire auxiliary electrode were used. Test solution (80 mL) was added into the cell and temperature was regulated via the thermostatted jacket to 25°C in all test work. Either oxygen (99.99%) or nitrogen (99.9%) was bubbled into the electrolyte for 10 min prior to starting the experiments. Subsequently, the electrodes were put in place and the desired test was started. Cyclic voltammetric and chronoamperometric tests were carried out using a Gamry Series G 300/750 Potentiostat.

**Open circuit potentials**

Open circuit potential measurements were made on the test solutions described above. The electrodes were allowed to equilibrate at open circuit in the solution for 30 minutes in all cases. The chalcopyrite working electrode was rotated at 1600 rpm, initial tests showed that rotation at this speed minimised mass transport related effects on the electrode. Potential-time transients were recorded, and the values reported and discussed in the Results section are the final potentials measured after 30 minutes. In each test, a freshly polished chalcopyrite electrode was used.

**Cyclic Voltammograms**

Cyclic voltammograms at a scan rate of 1 mV/s were generated immediately after the measurement of the open circuit potentials. The forward (anodic) sweep limit was set to 300 mV above the rest potential and it was then swept back to a cathodic limit of 250 mV below the rest potential. Only the anodic sweep part of the curves is presented and discussed here.

**Potentiostatic tests**

In anodic tests, the working electrode was freshly polished before the start of each run and rotated at 1600 rpm. Chrono-amperometric tests were run at the rest potentials or within the vicinity of rest potentials (as discussed in Moyo et al., 2015) previously measured in the presence of copper ions. This allowed for measurement of currents corresponding just to the anodic chalcopyrite dissolution in the relevant potential region in the absence of any oxidant or reductant in solution.

**Results and discussion**
Rest potentials of chalcopyrite were measured in the presence and absence of oxygen at varying initial copper concentrations. The results were presented in an earlier publication (Moyo et al 2015), but are reproduced here for clarity of the discussion (Figure 1). The data clearly indicates that the presence or absence of oxygen has no significant effect on the measured potentials. These rest potentials were established to be the mixed potentials of chalcopyrite under the specified solution conditions.

![Graph showing effect of varying initial copper(II) concentration on rest potential in 1M (NH₃+NH₄⁺) at 25°C (data from Moyo et al., 2015)](image)

**Figure 1.** Effect of varying initial copper(II) concentration on rest potential in 1M (NH₃+NH₄⁺) at 25°C (data from Moyo et al., 2015)

The anodic current was then measured by fixing the potential at the measured rest potentials in similar solution conditions as those in which the rest potentials were measured but in the absence of initial copper(II). Figure 2a shows the general trend of anodic currents measured at 255 mV SHE, that corresponds to the mixed potential in the presence of 5 g/L Cu(II). A sharp decrease in anodic current is observed during the first 5-10 minutes, and this is followed by what appears to be steady state current but in fact is a very gradual decrease over longer times (Figure 2b). A current spike at the onset of the test is expected and is due to the charging of the electric double layer. It is expected and accepted in literature (Warren et al 1982; Biegler and Swift, 1979) that chalcopyrite exhibits initially high currents which then decrease within minutes to significantly lower currents and this has often been linked to passivation of chalcopyrite. In the present study, the continued gradual decline in currents over long term experiments is related to the build-up of an iron based deposit layer as was shown by Moyo and Petersen (2016). However, the mineral surface did not passivate...
completely but only showed reduced currents, suggesting that the chalcopyrite oxidation continued, albeit at a slower rate.

Figure 2. Current–time transients at 255 mV SHE in 1 M (NH₃+NH₄⁺), 1600 rpm, pH 9.6 under nitrogen for 2 hrs (2a) and 20 hrs (2b). The potential is the mixed potential measured in similar solutions in the presence of 5 g/L Cu(II)

**Effect of potential on the anodic reaction**

The effect of potential on the anodic reaction has been evaluated using anodic sweeps as well as by running chronoamperometric tests. The anodic sweeps give transient data while chronoamperometric results give current densities that approximate steady state behaviour. Figure 3 presents plots of current density (after 2 hours of oxidation at constant potentials) as a function of the potential. The anodic sweeps can be seen in Figure 4 and Figure 5. In both types of tests, current densities can be seen to increase with an increase in potential as would be expected. It can also be seen that in some instances, in the presence of copper (Figure 5) the forward curve shows a slight peak below 250 mV, due to the oxidation of Cu(I) the product of chalcopyrite oxidation according to equation 2. Aside from the mentioned peak, the present study showed differences from the results of Warren and Wadsworth (1984) who under similar solution conditions and in a similar potential window observed some current peaks and troughs which they attributed to the formation of a number of passive intermediate layers. In the current study, there has been no indication that chalcopyrite passivates or forms intermediate passive layers.
Effect of potential on anodic current density after 2 hours at various potentials in 1 M (NH₃+NH₄⁺), 1600 rpm, pH 9.6 in the presence and absence of oxygen.

**Effect of total ammonia concentration**

Figure 4 shows the anodic current densities observed during potential sweeps at a scan rate of 1 mV/sec in solutions of varied total ammonia in the absence of initial copper(II). Anodic current densities were relatively low in 1 M total ammonia at all potentials, increased in 3M ammonia and were not significantly affected by an increase in total ammonia from 3 M to 6 M. Figure 5 shows the anodic current densities of chalcopyrite in solutions of varied total ammonia concentrations in the presence of 5 g/L initial copper (II). It can be seen that anodic current densities were not significantly affected by total ammonia at low potentials between 3 and 6 M, but increasing total ammonia resulted in an increase in current densities at high potentials. It should be pointed out that in all these studies the free ammonia available in solution was in excess of that required for the complexation of copper(II).
Warren and Wadsworth (1984) evaluated the effect of ammonia on the anodic reaction and reported increased anodic currents at a pH of 9.2 and low free ammonia concentrations from 0.028 M to 0.468 M. At relatively higher free ammonia concentrations, 1 M to 4.32 M and pH 10.24, they reported no dependence of the current on the free ammonia concentration at high potentials.
A close look at those results shows that Warren and Wadsworth (1984) neglected to mention the lower anodic currents observed at 1 M free ammonia at all potentials; hence the reported lack of a dependence can be considered true only for currents observed at concentrations between 1.61 and 4.32 M free ammonia.

**Effect of pH**

Anodic current densities appeared to increase with an increase in pH (Figure 6a and Figure 6b) in 1M total ammonia concentration. Warren and Wadsworth (1984) reported similar findings when measuring the response of the anodic current to pH changes. For aqueous solutions of ammonia the equilibrium between free ammonia and the ammonium ion is described by equation 4. As a result, the effect of pH on the reaction cannot be studied independently of changes in free ammonia concentration at a fixed total ammonia concentration. The solutions used in the current study contain low concentrations of Cu(II) and complexation of copper(II) by ammonia did not materially alter the free ammonia concentration.

\[ K_a = \frac{[NH_4^+][OH^-]}{[NH_3][H_2O]} \]

**Figure 6.** A – Current time transients of chalcopyrite oxidation at pH 9, 9.6 and 10 with the potentials set to 279 mV, 255 mV and 234 mV (corresponding to mixed potentials measured in similar solutions in the presence of initial copper(II)). B – anodic sweep measured at pH 9, 9.6 and 10

**Discussion**
Moyo et al (2015) established that the oxidative dissolution of chalcopyrite can be described by a mixed potential model. At the mixed potential, the oxidation and reduction reactions occur simultaneously on the chalcopyrite surface i.e. the sum of the currents due to the oxidation of chalcopyrite ((2) and/or (3)) is equal and opposite to the sum of the currents due to the reduction of copper(II) ions and dissolved oxygen. The anodic currents (using equation 2) can be written in terms of the high-field approximation of the Butler-Volmer equation;

\[ i_{\text{CuFeS}_2} = 7Fk_{\text{CuFeS}_2}[\text{OH}^-]^a[\text{NH}_3]^b e^{(1-\alpha_{\text{CuFeS}_2})E/RT} \]  

in which \( k_{\text{CuFeS}_2} \) is an electrochemical rate constant, \( E \) is the potential, \( \alpha_{\text{CuFeS}_2} \) is the transfer coefficient and \( a \) and \( b \) are the reaction orders with respect to hydroxyl ions and free ammonia. The factor 7 relates to the number of electrons transferred in reaction (2) as was established by Moyo et al. (2015).

At a constant potential, the anodic current densities are proportional to \([\text{OH}^-]^a[\text{NH}_3]^b\).

\[ i_{\text{CuFeS}_2} \propto [\text{OH}^-]^a[\text{NH}_3]^b \]  

Taking logs of both sides,

\[ \log i_{\text{CuFeS}_2} = a \log[\text{OH}^-] + b \log[\text{NH}_3] + \log k \]  

in which \( k \) is a proportionality constant.

The hydroxyl ion concentration was calculated from the measured pH of the solutions. The free ammonia concentration was calculated using a mass balance of total ammonia and the equilibrium constant defined in (4). This equilibrium constant \( K_a \) varies significantly with ionic strength as shown by the data in Figure 6 (Martell and Smith, 2004). As a result, the free ammonia concentration had to be estimated using an iterative method in which the ionic strength was initially calculated using a value of the ammonium ion concentration corresponding to 50% of the total ammonia. This value was then used to estimate \( K_a \) using the correlation shown in Figure 7 which was, in turn, used to estimate a new ammonium ion concentration and thereby a revised ionic strength. This procedure was repeated several times until convergence.
Figure 7. Variation of the protonation constant for ammonia as a function of ionic strength at 25°C. (Data reproduced with permission from Martell and Smith, 2004)

The order of reaction with respect to ammonia and to pH, has been calculated by solving for $a$, $b$ and $k$ using Excel solver of equation (7) using data (negative-going sweep data) from Figure 4 and Figure 6b at potentials chosen so that the contribution of the cathodic current to the overall current is minimal. This data is summarized in (Table 2).

**Table 2. Effect of pH and free ammonia concentration on the measured anodic current densities at various potentials.**

<table>
<thead>
<tr>
<th>pH</th>
<th>Total (NH$_3$+NH$_4^+$) M</th>
<th>Calculated free NH$_3$ (M)</th>
<th>400 mV Log i(μAcm$^{-2}$)</th>
<th>450 mV Log i(μAcm$^{-2}$)</th>
<th>500 mV Log i(μAcm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>1</td>
<td>0.282</td>
<td>2.236</td>
<td>2.594</td>
<td>2.896</td>
</tr>
<tr>
<td>9.6</td>
<td>1</td>
<td>0.654</td>
<td>2.449</td>
<td>2.749</td>
<td>3.033</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>0.840</td>
<td>2.930</td>
<td>3.18</td>
<td>3.44</td>
</tr>
<tr>
<td>9.6</td>
<td>3</td>
<td>1.557</td>
<td>3.024</td>
<td>3.377</td>
<td>3.71</td>
</tr>
<tr>
<td>9.6</td>
<td>6</td>
<td>1.051</td>
<td>2.835</td>
<td>3.22</td>
<td>3.65</td>
</tr>
</tbody>
</table>
Table 3 shows the calculated order of reaction at the different potentials. Given the limited amount of data, the order of reaction with respect to the hydroxyl ion can be assumed to be zero while that with respect to the concentration of free ammonia is close to 1. This is contrary to results presented by Warren and Wadsworth (1984) who reported no dependence of the current on free ammonia at high potentials (0.4 V–1 V).

<table>
<thead>
<tr>
<th>E (mV vs SHE)</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.22</td>
<td>0.92</td>
</tr>
<tr>
<td>450</td>
<td>0.04</td>
<td>1.09</td>
</tr>
<tr>
<td>500</td>
<td>0</td>
<td>1.19</td>
</tr>
</tbody>
</table>

A plot of the data at a constant pH of 9.6 is shown in Figure 7. Although there are only three points, it appears that the rate is linearly dependent on the ammonia concentration as suggested by the results in Table 3. Additional data would be required to confirm the dependence of the anodic oxidation rate on the ammonia concentration at lower concentrations.

Figure 8. Effect of the free ammonia concentration on the current at various potentials at a fixed pH of 9.6.
Tafel analysis (Figure 9) of the data presented in Figure 4 and Figure 6b

give reasonably linear plots. The mean Tafel slope was used to estimate a value for the charge transfer coefficient that varied from 0.53 to 0.69 with a mean value of 0.61. This value of the transfer coefficient is reasonably close to 0.5 that suggests that the rate determining electron transfer step involves a single electron (Guidelli et al, 2014). As pointed out by Guidelli et al (2014), values of 0.5 are only generally observed for simple electron transfer reactions involving minor reorganization of the reacting species and could not be expected in this case.

A possible single electron rate-determining reaction that would be first-order in ammonia is

\[ \text{CuFeS}_2 + \text{NH}_3 = \text{Cu(NH}_3) + (\text{FeS}_2) + \text{e} \]

with subsequent rapid reactions involving further complexation of the mono-ammine and transfer of the remaining 6 or 7 electrons. The above should not be read to imply that actual pyrite is a product but simply to suggest that the surface is copper-deficient—it is for this reason that FeS₂ was written in brackets.

Conclusions

The anodic oxidation of chalcopyrite has been shown to be of 1st order dependence on free ammonia between 0.28 M and 1.56 M free ammonia concentration. Chalcopyrite oxidation was concluded to have zero order dependence on [OH⁻] at a pH between pH 9 and pH 10. The calculated charge transfer coefficient was found to be reasonably close to 0.5, and thus it is concluded that the rate determining step is a single electron transfer reaction. This single electron reaction could be that of the oxidation of copper from the chalcopyrite lattice forming a copper depleted surface.
which is rapidly oxidised in subsequent coulomic reactions on the mineral surface. Constant potential data has not supported theories of passivation or formation of intermediate passive surfaces, however the observed reduced anodic currents support the theory that the surface deposit forming during the reaction is non-passivating but hinders the rate of dissolution.

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