Open Circuit Potential and Leaching Rate of Pyrite in Cupric Chloride Solution

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Abstract.

As a refractory gold mineral, pyrite need to be oxidized prior to gold leaching. In this study, the effect of $[Cl^-]$ concentration (40.6-149.8 g/L), $[Cu^{2+}]$ concentration (0.8-31.6 g/L), pH (1.5-2.5) and temperature (25-90 °C) on the pyrite leaching rate was investigated. In addition, the OCP values of pyrite in cupric chloride solution were investigated.

A linear regression model was constructed to predict pyrite dissolution rate i.e. corrosion current density. It was shown that temperature had a significant positive effect on pyrite dissolution, whilst increase cupric ion concentration were also shown to provide some dissolution enhancement. According to the regression analysis, pH had no effect on the corrosion current density at OCP. Dissolution rates of pyrite varied between 0.05-2.9 µm/h. The activation energy values from 20 to 90 kJ/mol, indicated that the pyrite dissolution reaction rate was controlled by the chemical reaction or mixed mechanism rather than diffusion alone. The simultaneous increase in corrosion potential and corrosion current density indicated that the anodic pyrite dissolution reaction was rate determining at OCP.

Keywords: pyrite, cupric chloride, sodium chloride, anodic polarization, corrosion current density

1 Introduction

Pyrite is a refractory gold mineral and may contain significant amounts of gold enclosed in its mineral matrix. Industrially, pyrite is oxidized to destruct the mineral matrix for gold liberation by e.g. roasting (La Brooye et al. 1994, Filmer, 1982), pressure oxidative leaching (POX) (Papangelakis & Demopoulos, 1991, Long & Dixon, 2004) or bioleaching (van Aswegen, et al. 2007, Groza et al. 2008). Since 1890s the prevailing technology for gold leaching has been cyanide leaching (Rose, 1989, Marsden & House, 2006). However, alternative methods for gold leaching are being developed. In the development stage chloride processes, the oxidative power of the solution in controlled by high chloride and cupric ion concentrations (Lundström, et al. 2009) rather than chlorine gas used in the historical chlorination processes (Rose, 1898). The advantage of cupric chloride leaching of pyrite is that refractory mineral oxidation and gold dissolution can be conducted simultaneously in a single stage process at atmospheric pressure (Miettinen et al. 2013) rather than separately e.g. by cost intensive pressure oxidation and cyanidation. In the future this can provide a competitive cyanide free one-stage gold leaching process for refractory gold ore. Cyanide-free gold leaching has been operated in demonstration scale in processes such as...
Nippon N-Chlo (Ishiguro et al. 2008), HydroCopper (Haavanlammi et al. 2007), Outotec Gold Chloride process (Miettinen et al. 2013), Dundee (Lalancette, 2009, Lemieux et al. 2013), Intec (Moyes & Houllins, 2010), Platsol (Ferron et al. 2003), and Neomet (Harris & White, 2014). Nippon, Intec, HydroCopper, and Platsol process motivation originated initially from leaching of sulfidic ores to recover base metals with minor gold.

Electrochemical methods such as cyclic voltammetry, potentiostatic and –dynamic, galvanostatic and –dynamic methods as well as electrochemical impedance spectroscopy can be used to investigate electrochemical phenomena related to interaction of sulfide minerals and the solution matrix (Lundström et al. 2005, Lundström et al. 2008).

Pyrite is a relatively noble sulfide mineral creating galvanic currents and accelerating the dissolution of other sulfide minerals such as chalcopyrite (Ruiz, et al. 2015). During acidic pressure oxidation potentials over 480 mV vs. Ag/AgCl are known to dissolve pyrite (Littlejohn & Dixon, 2008, Rusanen et al. 2013). Pyrite leaching in cupric chloride solutions can be suggested to follow Equation (1), which can be divided to partial reactions (2) and (3).

\[
\text{FeS}_2(s) + 3[\text{CuCl}]^{+}(aq) + 8\text{Cl}^{-}(aq) \rightarrow [\text{FeCl}_2]^{+}(aq) + 3[\text{CuCl}_3]^{-2}(aq) + 2S_0(s) \quad (1)
\]

\[
\text{FeS}_2 + 2\text{Cl}^{-} = \text{FeCl}_2^{+} + 2S_0^{0} + 3e^{-} \quad (2)
\]

\[
\text{CuCl}^{+} + 2\text{Cl}^{-} + e^{-} = \text{CuCl}_3^{-2} \quad (3)
\]

According to the authors knowledge, the research detailed here outlines, for the first time, an electrochemical investigation of pyrite open circuit potential (OCP) in cupric chloride solution and the corresponding pyrite dissolution rate as a function of parameters \(T, pH, [\text{NaCl}], [\text{Cu}^{2+}]\), and the combined effect of these parameters.

## 2 Materials and experimental procedure

In the current study, dissolution of pyrite in cupric chloride media was investigated by polarization experiments. The OCP and dissolution rate were determined from the polarization curves.

2.1 Materials, experimental conditions and set-up

The pyrite sample originating from South America, Peru was used as a working electrode (WE) \((A = 0.7-1.3 \text{ cm}^2, R = 25 \Omega)\). Experiments were conducted in a standard electrochemical three-electrode cell \((V = 200 \text{ ml})\) with standard calomel (Radiometer, Ref401) as reference electrode (RE) and platinum as counter-electrode (CE). Magnetic agitation and nitrogen purging (2 bar) was applied. ACM Instruments Gill AC potentiostat controlled by Gill AC Sequencer was applied to run a half cycle sweep from 300 mV to 900 mV vs. SCE with a sweep rate of 50 mV/min.

The pyrite electrode surface was polished prior to every measurement. Regression analysis was conducted to predict the effect of measured parameters \((T, [\text{Cu}^{2+}], [\text{Cl}^{-}], \text{pH})\), see Table 1) on OCP and corrosion current density (MODDE 8.0 software (Umetrics, 2016)).
Table 1. Solution compositions and the investigated pH and temperature levels used in the pyrite leaching experiments. 135 experiments (full factorial series) were conducted in total.

<table>
<thead>
<tr>
<th>[Cu$^{2+}$] (g/L)</th>
<th>[Cl$^{-}$] (g/L)</th>
<th>pH</th>
<th>$T$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>49.8, 91.2, 149.8</td>
<td>1.5, 2, 2.5</td>
<td>25, 45, 60, 75, 90</td>
</tr>
<tr>
<td>15.8</td>
<td>45.3, 91.2, 145.3</td>
<td>1.5, 2, 2.5</td>
<td>25, 45, 60, 75, 90</td>
</tr>
<tr>
<td>31.6</td>
<td>40.6, 91.2, 140.6</td>
<td>1.5, 2, 2.5</td>
<td>25, 45, 60, 75, 90</td>
</tr>
</tbody>
</table>

2.2 Methods

Activation energy presents the correlation between temperature and the reaction rate, and can be presented in the form of equation (4).

$$\ln(k_2) - \ln(k_1) = -\frac{E_a}{R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$  (4)

where, $k$ is current density, $A$ is frequency factor, $E_a$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature. The activation energy was determined by fitting $\ln(k)$ vs. $1/T$. The slope ($-\frac{E_a}{R}$) and the value of the activation energy can indicate the reaction rate controlling mechanism (Peters, 1973).

Tafel method was used to calculate the pyrite dissolution rate at OCP, equation 5. The Tafel slopes were determined ACM Analysis software.

$$\eta = a + b \cdot \log(i)$$  (5)

in which the $a$ and $b$ are the Tafel coefficients, $a$ describing current density and the coefficient $b$ is the Tafel slope (mV/decade).

In this study, MODDE 8.0 software was used to build the linear regression model. Temperature was presented as $1/T\times1000$ form and the corrosion current densities were presented as log ($j$). The MODDE analysis was conducted in two steps; determination of scaled and centered coefficients and transforming them to unscaled coefficients. An equation describing the effect of parameters on a research subject was built based on the significant coefficients.

3 Results

3.1 Linear regression model for pyrite OCP in cupric chloride solution

The OCP values were shown to vary from 380 to 525 mV vs. SCE. The results showed that OCP increased as a function of temperature in the range of 25-90 °C. Moreover, higher cupric ion concentrations indicated generally higher OCP values and chloride ion concentration was observed
to have little effect on OCP. No clear trend for the effect of pH on OCP was found. This again suggests that the cathodic cupric reduction reaction (reaction 3) increases during cupric chloride leaching more than anodic pyrite dissolution reaction (reaction 2), suggesting that anodic reaction rate determines the dissolution of pyrite.

The OCP values from the anodic polarization measurements were fitted in a linear regression model for the evaluation of the effect of investigated parameters on OCP. Figure 1 presents the scaled and centered coefficients of the investigated parameters based on the data. It can be seen (Figure 1) that the significant coefficients affecting the OCP of pyrite in chloride solution were temperature, concentrations of cupric and chloride ions, pH, and the combined effect of temperature and cupric ion concentration. Other combined effects were shown not to be valid. Thus, equation (6) could be formed to predict the effect of investigated parameters on pyrite OCP vs. SCE in cupric chloride solution. The regression model performance indicators (R² = 0.812, Q² = 0.796, model validity = 0.338 and reproducibility = 0.946) were shown to reach the reference values (Eriksson et al., 2008) for the model to be valid.

Pyrite OCP = 352.112 + 0.335789 ∙ T + 1.42409 ∙ [Cu²⁺] + 0.543719 ∙ [Cl⁻] -10.7364 ∙ pH + 0.0190053 ∙ T ∙ [Cu²⁺]

In which T is temperature in °C, [Cu²⁺] is cupric concentration as g/L, [Cl⁻] is chloride concentration as g/L, pH is pH value and OCP is vs. SCE. The predicted vs. measured values all suggests a linear fit of correlation.

3.2 Model for pyrite dissolution rate at OCP

Pyrite dissolution rate at OCP was determined using Tafel method. Figure 2 presents the dissolution rate calculated from polarization measurements. It can be seen that increasing the cupric ion concentration and temperature increased the dissolution rate of pyrite at OCP. The
highest dissolution rates were achieved at the highest temperature using the highest cupric ion concentration. The results indicated that chloride concentration had a statistically insignificant effect on the pyrite dissolution rate at OCP.

![Graph showing dissolution rate as a function of temperature and cupric ion concentration.]

Figure 2. The dissolution rate of pyrite at OCP. The dissolution rate is presented as a function of temperature and cupric ion concentration.

Pyrite dissolution rate was shown to follow the Arrhenius equation. The activation energies varied in the range of 20-90 kJ/mol at OCP and also when polarized to 600 mV vs. SCE. This indicates that the pyrite leaching reaction in concentrated cupric chloride solution was under mixed or chemical control rather than diffusion (Peters, 1973).

The analysis showed that the significant parameters affecting pyrite dissolution rate were \([Cu^{2+}]\), \([Cl^-]\), \(T\) and the combined effect of \([Cl^-]\) & \(T\). The effect of pH was studied at three different values (1.5, 2 and 2.5), however the effect was shown not to be statistically valid and thus this parameter was not included the model. The model performance indicators (R2 = 0.825, Q2 = 0.811, model validity = 0.517, and reproducibility = 0.927) were compared to acceptable model values (Eriksson et al. 2008) and the values showed that the model built for pyrite leaching in cupric chloride solution was valid.

Based on the regression analysis an equation (7) was formed for pyrite dissolution at open circuit potential in cupric chloride solution.

\[
\log(j) = 6.428 + 0.0064262 \cdot [Cu^{2+}] – 0.012323 \cdot [Cl^-] – 2.54993 \cdot 1/T \cdot 1000 + 0.00495225 \cdot [Cl^-] \cdot 1/T \cdot 1000
\]  

(7)
where, \( T \) is temperature in K, \([Cu^{2+}]\) is cupric ion concentration in g/L and \([Cl^-]\) is chloride concentration in g/L.

It can be seen that increasing temperature and cupric ion concentration increases the pyrite corrosion current density i.e. dissolution rate. In addition, the increase in the chloride ion concentration and temperature has a clear increasing effect on the corrosion current density.

The models built show that increasing copper concentration and temperature increases the corrosion potential and corrosion current density. The increasing corrosion current density with increasing OCP indicates according to mixed potential theory (Robertson et al. 2005) that increasing \( T, [Cu^{2+}] \) and \([Cl^-]\) increased the cathodic reaction rate more than the anodic reaction rate. Furthermore, the chloride ion concentration has increasing effect as combined parameter with temperature. The simultaneous increase in corrosion potential and corrosion current density indicates according to the mixed potential theory, the cathodic reaction (Equation 3) rate increases faster than the anodic reaction (Equation 2), the latter limiting the pyrite dissolution rate at OCP.

Figure 3. The effect of cupric ion concentration and temperature to pyrite corrosion current density according to the model using MODDE 8.0. \([Cl^-] = 149.8 \text{ g/L, temperature is presented as } 1/T \text{ form and multiplied by 1000 and the corrosion current density is expressed as } \log(j)\).
The modelled corrosion current densities correspond to pyrite dissolution rates of 0.05-2.9 µm/h in the investigated parameter range. Figure 4 presents the correlation between the dissolution rates and the OCP. The highest dissolution rate (2.9 µm/h) could be achieved only at highest \([Cu^{2+}]\) concentration and temperature (\([Cu^{2+}] =31.6\) g/L and \(T=90\) °C). With \([Cu^{2+}] = 0.8\) g/L, the highest dissolution rate according to model is 1.9 µm/h. The highest temperature (\(T = 90\) °C) was required to achieve dissolution rate over 2.0 µm/h.

![Figure 4. A plot of dissolution rate vs. OCP as function of cupric ion concentration at all conditions used in the modelling and calculated by the model constructed. The dissolution rate is calculated from the corrosion current densities, which are calculated with the model.](image)

**4 Conclusions**

The interest for pyrite chloride leaching lies in the possibility to simultaneously oxidize pyrite and leach gold in a single process unit, without a need for pre-oxidation through POX, roasting or bio-oxidation. In this study, the dissolution of pyrite in cupric chloride solutions was investigated by electrochemical methods. The effect of \([Cu^{2+}], [Cl^-], \) pH and \(T\) and the combined effect of these on pyrite OCP and pyrite corrosion current density were investigated.
Temperature was found to have increasing effect on the pyrite OCP, values varying in the range 380-525 mV vs. SCE. Furthermore, with increasing $[Cu^{2+}]$ and $[Cl^-]$ concentration the OCP was shown to increase. The pH had an insignificant effect on the OCP.

OCP and pyrite dissolution rate models were formed based on polarization measurement data. According to the OCP model, temperature, cupric and chloride ion concentration and the combined effect of $T$ and $[Cu^{2+}]$ had a positive i.e. increasing effect on the OCP whereas pH was found to have a negative effect. Additionally, the effect of studied parameters to corrosion current density i.e. pyrite dissolution rate was evaluated. The results indicated that temperature had a major positive effect on pyrite dissolution rate. In addition, $[Cu^{2+}]$ concentration and the combined effect of $[Cl^-]$ concentration and temperature had a minor positive effect on pyrite dissolution rate. $[Cl^-]$ concentration as an individual parameter had a minor negative effect. The effect of pH was not statistically valid and was excluded from the model. The measured corrosion current densities corresponded to pyrite dissolution rates of 0.05 – 2.9 µm/h. The model performance indicators (R2, Q2, model validity, and reproducibility) were acceptable in both OCP and pyrite dissolution models confirming that the models were valid. The models built for pyrite OCP and pyrite corrosion current density at OCP can be used to predict the dissolution of pyrite in the investigated parameter range, pH = 1.5-2.5, $[Cu^{2+}] = 0.8-31.6$ g/L, $[Cl^-] = 40.6-149.8$ g/L and $T = 25-90$ °C.

Furthermore, the activation energy of pyrite dissolution was investigated and was found to be in the range of 20-90 kJ/mol, indicating mixed or chemically controlled reaction mechanism in cupric chloride solution. Both experimental data and the models built showed that OCP and corrosion current density increased as a function of chloride ion concentration (40.6-149.8 g/L), cupric ion concentration (0.8-31.6 g/L) and temperature (25-90 °C). According to mixed potential theory this indicates that the cathodic cupric reduction reaction rate increased faster compared to anodic pyrite dissolution reaction. This suggests that the anodic reaction rate was the rate controlling step in the cupric chloride leaching of pyrite.

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5 References


