GALVANIC ENHANCEMENT FOR HIGH PRESSURE LEACHING OF CHALCOPYRITE

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Abstract

This study was conducted to evaluate the galvanic enhancement of the pressure oxidation (POX) leaching of a chalcopyrite/chalcocite concentrate, which is believed to take place via a redox reaction. Cu recoveries of > 90% could be achieved during POX leaching of this chalcopyrite/chalcocite concentrate at 200°C and 0.7 MPa initial oxygen pressure within 2 h in a pressure reactor lined with titanium, which were 18-28% higher than for the same leaching using the teflon liner. A slow heating time seems to produce more sulphur coating, reducing the leaching performance, yielding much lower Cu recovery when the teflon lining was used, although this does not greatly affect the other case when the reactor was lined with titanium. The introduction of an electronic conductor, in this case the titanium surface, is believed to enhance this redox process, in which the oxidation of copper minerals and sulphur to sulphate at the anodic sites (mineral surface) encountered during POX leaching takes place simultaneously with the reversible oxidation/reduction of the Fe²⁺/Fe³⁺ couple and oxygen reduction on titanium.

Keywords: Pressure oxidation; Chalcopyrite; Galvanic; Redox reactions

1. Introduction

Pressure oxidation (POX) at elevated temperature (110-225°C) and pressure (0.4-3 MPa) has been widely used for oxidising pyrite to liberate gold and precious metals from refractory ores for further processing. The technology has been practised for over 20 years [1] at Lihir (PNG), Porgera (PNG) and MacCraes (NZ) mines to recover gold from refractory pyritic ores. POX is also applied for processing nickel and copper sulphide concentrates. Atmospheric leaching of chalcopyrite in sulphate and chloride media up to 100°C has also been studied in several investigations and reviewed recently by Watling [2]. Table 1 summarises well-developed POX technologies treating copper sulphide concentrates, showing processing conditions including temperature, oxygen pressure, Pₘ₀ (80% passing size) and different additives. A number of technologies have been trialled at demonstration or semi-commercial scale for processing copper concentrates using POX [3-6].

With POX at a low or intermediate temperature (110-150°C) the sulphide minerals are oxidised to produce dissolved copper and sulphur. Additives such as NaCl [8],coal and surfactants [9] have been used to minimise the oxidation of sulphur to sulphate or to prevent its coating of unreacted particles, thus increasing the metal recovery from the leaching. Based on this the Activox process has been tested at Tati Mines [7-9] for producing 25,000 tpa Ni and 22,000 tpa Cu before being suspended in 2007. The CESL process promoted by Cominco Engineering Services Ltd was also tested at Vale in 2008 for the production of 10,000 tpa LME Cu [14]. Addition of 12 g/L chloride was used to ensure the 90% of sulphide conversion to sulphur thus minimising the sulphuric acid generation. The operation at Sepon Mine (by MMG) employs POX at 225°C and 3 MPa oxygen pressure to oxidise pyrite to produce sulphuric acid and the ferric iron-containing solution used for the leaching of chalcocite concentrate in a subsequent stage. High temperature (225°C) and oxygen pressure (3 MPa) were also used in a POX process producing 16,000 tpa LME Cu at Morenci plant (Freeport McMoRan/Phelp Dodies) in Bagdad, Arizona (USA). The semi-commercial plant which started in 2003 was subsequently shut down in 2007 [6].

Watling [2,19] reviewed the chemistry of different processes used for chalcopyrite treatment, including acidic sulphate or chloride leaching. The overall electrochemical reactions involve both oxygen at the beginning and Fe⁷⁺ subsequently produced from the
leaching of chalcopyrite and the mineral particles. At low and intermediate temperatures up to ~150°C sulphur is mainly formed whereas complete oxidation of sulphur forming acidic sulphate occurs at higher temperatures. The electrochemical half-cell reactions taking place at the initial stage of leaching can be represented by:

\[
\text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{S}^2- + 4e^- \quad \text{(anodic)} \quad (1)
\]

\[
\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad \text{(cathodic)} \quad (2)
\]

The Fe\(^{2+}\) formed is further oxidised by oxygen forming Fe\(^{3+}\), which subsequently oxidises chalcopyrite according to:

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \quad \text{(anodic)} \quad (3)
\]

\[
4\text{Fe}^{3+} + \text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + 5\text{Fe}^{3+} + 2\text{S}^2- \quad (4)
\]

At a high temperature and pressure used in POX, sulphur (S\(^0\)) is also oxidised to sulphate(SO\(_4^{2-}\))generating acid according to:

\[
\text{S}^0 + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 8\text{H}^+ + 6e^- \quad \text{(anodic)} \quad (5)
\]

Under these conditions, Fe\(^{3+}\) can precipitate forming hematite, the main iron product from POX:

\[
2\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 6\text{H}^+ \quad (6)
\]

The leaching of chalcopyrite at both low (<80°C) and intermediate temperature (110°C) is enhanced by the addition of Ag\(^+\)(at 1g Ag/kg Cu in chalcopyrite) forming Ag\(_2\)S on the chalcopyrite surface [2,20,21]. However, the mechanism suggested by Cordoba et al. [20] that Ag\(^+\) is the oxidant responsible for the oxidation of chalcopyrite and the silver sulphide is then oxidised by Fe\(^{3+}\) was questioned [2]. The addition of pyrite to a chalcopyrite leach [22,23] or silver-incorporated pyrite was also observed to enhance the reaction rate and leaching of chalcopyrite [24]. The presence of the pyrite surface with higher electronic conductivity acting as cathodic site for oxygen and Fe\(^{3+}\) reduction was suggested as the reason for such an enhancement. In this case, the collision of pyrite and chalcopyrite particles is believed to form a galvanic couple of cathodic and anodic sites. As a result, the initial reduction of oxygen (Eq. 2) on pyrite and oxidation of chalcopyrite (Eq. 1) would take place simultaneously. This galvanic couple facilitates the electron transfer between the chalcopyrite as anode to pyrite as cathode. As more Fe\(^{3+}\) is formed it can also react with chalcopyrite (Eq. 4) directly or via the pyrite-chalcopyrite galvanic couple. This is the basis for the Galvanox process [24,25].

Most laboratory studies on POX however have been conveniently undertaken in a titanium pressure vessel and the leaching performance (reaction rates and yields) could differ from that experienced in commercial installations. In this respect, the materials used in a POX-autoclave system using steel vessels lined with lead, ceramic, teflon or wood materials would affect the leaching of chalcopyrite [26]. This paper therefore aims to address the galvanic effect of different metallic additives and/or reactor materials on the copper extraction and reaction rate of chalcopyrite leaching.

2. Experimental

2.1 Materials

The feed used for the study was a “below-commercial grade” copper sulphide concentrate produced from a low grade ore. Analysis of digested

<table>
<thead>
<tr>
<th>Process</th>
<th>Temp (°C)</th>
<th>O(_2) Pressure (MPa)</th>
<th>P(_{80}) (μm)</th>
<th>Additives</th>
<th>Note / References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activox</td>
<td>110</td>
<td>1.1</td>
<td>7</td>
<td>2-10 g/L Cl</td>
<td>70% S yield, tested at Tati Mines for 25,000 tpa Ni, 22,000 tpa Cu [7-9]</td>
</tr>
<tr>
<td>NSC</td>
<td>125</td>
<td>0.4</td>
<td>~20</td>
<td>2 g/L Na nitrite</td>
<td>[8-11]</td>
</tr>
<tr>
<td>Anglo-UBC</td>
<td>150</td>
<td>1.2</td>
<td>7</td>
<td>Surfactant</td>
<td>70% S yield [8,9,12,13]</td>
</tr>
<tr>
<td>CESL</td>
<td>150</td>
<td>1.2</td>
<td>37</td>
<td>12 g/L Cl</td>
<td>90% S yield. Plant operated by Vale, 10,000 tpa Cu [14]</td>
</tr>
<tr>
<td>Dynatec</td>
<td>150</td>
<td>1.2</td>
<td>37</td>
<td>25 kg/t coal</td>
<td>[10,15]</td>
</tr>
<tr>
<td>Sepon-MMG</td>
<td>225</td>
<td>3</td>
<td>100</td>
<td>Pyrite POX to produce Fe(III)–acid for chalcocite leaching at 80°C, 80,000 tpa Cu since 2011 [16,17]</td>
<td></td>
</tr>
<tr>
<td>Cobre Las Cruces</td>
<td>140-225</td>
<td>3</td>
<td>13-15</td>
<td>Phelps Dodge/Freeport’s Morenci plant 16,000 tpa Cu (now closed) [18]</td>
<td></td>
</tr>
</tbody>
</table>
sample by ICP-AES presented in Table 2 shows major
components in the ore feed. As later shown in Fig. 1
the low grade concentrate contains chalcopyrite,
chalcocite, pyrite,feldspars (albite) and quartz as
major mineral phases.

Table 2: Components of feed material used in this study
(Analyzed by ICP-OES)

<table>
<thead>
<tr>
<th>Component</th>
<th>Cu</th>
<th>Fe</th>
<th>Na</th>
<th>Al</th>
<th>K</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>9.25</td>
<td>7.21</td>
<td>4.51</td>
<td>9.1</td>
<td>5.13</td>
<td>0.82</td>
</tr>
<tr>
<td>Component</td>
<td>Mg</td>
<td>Mn</td>
<td>Zn</td>
<td>As</td>
<td>Si</td>
<td>S</td>
</tr>
<tr>
<td>%</td>
<td>0.44</td>
<td>0.031</td>
<td>0.076</td>
<td>0.042</td>
<td>21.9</td>
<td>7.6</td>
</tr>
</tbody>
</table>

X-Ray Fluorescence analysis of several samples of
the feed material confirmed the composition range of
8.2-9.2% Cu, 6.2-7.2% Fe, 5.6-7.6% S and 21.8-
22.2% Si. Via XRF analysis the sum of all analyses as
oxide totals 102%, which is accurate for the material
tested.

2.2 Equipment and chemicals

Cu and Fe chemical analysis was conducted using
AAS (Varian AA220). The mineralogy of the feed
material and products was determined by X-Ray
Diffraction (XRD) analysis (X’Pert PRO MultiPurpose
X-Ray Diffractometer, PANalytical) where their compositions were also determined by
XRF using an instrument from PANalytical. Energy-
Dispersive Spectrometry (EDS) study was conducted
to map the elemental distribution in samples before
and after leaching using a Bruker-AXS (XFlash
5020).

All chemicals used in this study were of analytical
grade including sulphuric acid (98% w/v) and aqua
regia. Double deionised water was used for the
experiments.

2.3 Procedures

The pressure oxidation experiments were
conducted using a stainless steel pressure vessel
heated by an electrical jacket. Two inserts made from
teflon and titanium were used for the study, with the
teflon lining representing an inert reactor environment
whereas titanium can act as an electronic conductor
during the leaching. The slurry was well suspended by
an agitated impeller coated with Teflon, at a rate of
200 rpm. The reaction temperature was measured by
an immersed thermocouple and the slurry could be
cooled down quickly within 10 min using a water
cooling coil inside the reactor. Pure oxygen used for
the experiments was introduced from a cylinder and
regulated by a valve and a gauge at the outlet to
monitor the gas pressure. The gas pressure during the
experiment was also monitored by a finer pressure
gauge directly linked to the reactor. At the start of the
experiment, the slurry made from a known mass of the
feed material and weighed quantity of 5 g/L sulphuric
acid (100 g solid/L leach liquor) was introduced into
the reactor at ambient temperature. The vessel was
then closed and flushed with oxygen for 5 minutes to
fill the air gap above the slurry before pressurising it
to 0.7 MPa at ambient temperature. With all valves
closed to ensure the oxygen quantity introduced
would not change, the reactor was then heated at
different heating rates (heating time: 13-100 min as a
parameter for this study) until the test temperature in
the range 180-200°C was reached. By then, depending
on the temperature, the total system pressure reached
2-2.5 MPa. At the reaction temperature, the
experiments were then conducted for various fixed
times (30, 60, 90 or 120 min), after which the reactor
was cooled down to ambient temperature quickly.
After the experiments, the slurries were filtered to
recover the leached residues which were washed in
water and dried in an oven at 90°C before samples
were collected and divided for various analyses
(XRD, XRF). Weighed samples of the feed material
and residues were then digested in aqua-regia to
confirm the Cu and Fe content by chemical analysis
using AAS. The Cu and Fe extraction percentages
were calculated from the chemical analyses of leached
liquors and average digested feed materials.

3. Results and discussion

One of the aims of the study is to determine and
quantify, if any, the effect of an electrochemical
conductor or surface on the extraction of copper
during POX leaching of copper sulphide minerals. In
this respect, the teflon insert provides an inert lining to
completely isolate the slurry from any electronic
conductor whereas the titanium insert provides a
surface for electron exchange that may assist the
electrochemical dissolution of sulphide particles by
the oxidants (Fe³⁺ and/or dissolved oxygen). Different
parameters were studied including heating time,
reaction time, particle size and temperature. It is
known that the initial stage of the pressure oxidation
requires much acid to start the reaction and in several
studies up to 50 g/L sulphuric acid was added initially
[9]. However, in this study an initial 5 g/L sulphuric
acid was added to allow the reaction to proceed more
slowly for easier observation of the galvanic effect.

3.1 Feed and residue material characterisation

Fig. 1 compares the XRD patterns of the
concentrate feed used in the study and the residues
collected after the experiments using Ti or teflon
linings. XRD analysis confirms the presence of
chalcopyrite (CuFeS₂) and chalcocite (Cu₂S) as main
Cu minerals whereas iron mainly exists as pyrite. After POX, the remaining unreacted copper mineral was identified as covellite (CuS). Most iron was converted to hematite and the main gangue mineral identified arealbite (silicate containing Ca, Al and Na) and illite (silicate containing K and Al). At low Na (2.31% Na₂O) in the feed the formation of sodium-jarosite was not detected at the pulp density used (100 g solids/L liquor). As reviewed by McDonald and Muir [8,9] jarosite is believed to be formed at moderate or high acid concentration (50 g/L H₂SO₄ initial concentration vs 5 g/L acid used in this study), in the presence of high Na and low pulp density, which are not the conditions of this study. No elemental sulphur was detected in XRD patterns of residues produced at different heating or reaction time, either using Ti or teflon-lined reactors.

### 3.2 Effect of heating rate

One concern during oxygen pressure leaching of sulphide minerals has been the formation of sulphur in the temperature range 120-180°C, leading to the passivation of the reaction due to its coating of the sulphide particles. Various surfactants (sodium lignosulphonate, etc.) can be used to alleviate this effect [9] although pressure leaching at high temperature (200-220°C) appears to eliminate this problem as all sulphur should be oxidised to sulphate. However, it is not known whether a sulphur coating can be completely oxidised if it were formed during a long heating period before the reaction temperature is reached. Various heating times in the range 13-100 min to reach a fixed reaction temperature of 200°C (shown in heating profiles of Fig. 2) were tested to

![Figure 1](image)  
**Figure 1.** XRD patterns for concentrate feed and residues using titanium (Ti) or teflon (Tf)-lined reactors obtained at different heating (H) and reaction time (R). Other test conditions: D₉₀ = 16.49 µm, initial O₂ pressure: 0.7 MPa  
(Caption note: Tf-H20-R120: Teflon-lined reactor, heating time: 20 min, Reaction time: 120 min)
determine the impact upon copper and iron extractions and the results are shown in Figs 3a and b.

As indicated in Fig. 3a, a Cu recovery of 93% was achieved for a fast heating time (13 min) to reach the reaction temperature of 200 °C with 60 min extra reaction time at this temperature. In all cases where the heating time was varied within the range 13-100 min there was a slight drop in Cu recovery for the experiments conducted with the Ti lining (from 93.0% to 88.1%). On the other hand the Cu recovery was 74.1% for a fast (high) heating time of 20 min but dropped much more to 59.0 % at a slow (low) heating time (100 min) when the teflon lining was used. Iron was extracted more into solution when the teflon-lined reactor is used in all cases.

To isolate the Cu and Fe extracted during heating, a series of experiments was conducted to observe their extractions at different heating time and zero reaction time. As shown in Fig. 3b, 40-60% of Cu was already extracted within the heating time range 13-100 min, when the Ti reactor was used. On the other hand, using teflon-lined reactor, the Cu extracted was constant at ~30% extraction, independent of the heating time in the range 20-100 min. Again, more Fe was extracted during heating in the time range 20-100 min, using teflon-lined reactor. The results shown in Fig. 3b indicate that the oxidation of Fe2+ to Fe3+ is also promoted by using Ti reactor. This would lead to faster precipitation of hematite when Ti reactor was used, leading to lower extraction of Fe into solution. A long heating period also seems to create conditions so that iron does not precipitate as efficiently to hematite. As a result the level of dissolved iron reached 12% and 30% of the extractable amounts for the Ti and teflon lining experiments, respectively. In most cases at other conditions, less than 10 % soluble iron still remained in the liquor after POX leaching of the copper concentrate when a fast heating rate (< 20 min) was applied.

3.3 Effect of different reaction time and particle sizes

Figs. 4a and b show the effect of reaction time for 2 particle sizes (D90 = 16.49 and 40.27 µm) tested under the same conditions (200°C, 0.7 MPa initial O2 pressure). With the Ti lining, the extraction of Cu reached 87.3, 91.7 and 93.0% in 60, 90 and 120 min, respectively, for the 16.49 µm material (Fig. 4a). On the other hand with the teflon lining the extraction of Cu reached 72.2, 76.4 and 81.3 % after the same periods, respectively, for the 16.49 µm material (Fig. 4a). On the other hand with the teflon lining the extraction of Cu only reached 72.2, 76.4 and 81.3 % after the same periods, respectively, for the same material. In all cases the finer material leaches quicker as expected, especially in the presence of the titanium surface. The extraction rate is expectedly lower for the coarser material (Fig. 4b) and again the Cu extraction is always lower for the experiments conducted with the teflon lining.
3.4 Effect of temperature

Fig. 5 shows the variation of the Cu extraction for the temperature range 150-220°C and reaction time 1 or 2 h. It seems that the Cu extraction of 87.3% at 1 h and 93.0% at 2 h at 200°C was not improved much at higher temperature in experiments using the Ti lining. However for the teflon lining experiments the Cu extraction still has not reached a steady state and continues to trend upward above 200°C. In the temperature range tested, the Cu recovery for the teflon lining experiments at the same conditions is 18-28% lower than for the Ti lining. For temperatures in the range 150-220°C, increasing the reaction time from 1 h to 2 h slightly improves the Cu extraction (5-8%). The level of dissolved Fe is less than 10% in most cases.

3.5 Effect of additives

The effect of using different metal additives in the experiments conducted with the teflon lining is shown in Fig. 6. The rationale behind this series of tests was to determine whether an addition of an electronic conductor into the slurry would enhance the Cu leaching performance. This would have a great implication for large scale POX systems (where a lead lining for the pressure vessels is commonly used) and cheap additives such as coal or charcoal can be used. Results indicate that additions (2-10 g/L) of carbonaceous materials such as charcoal, activated carbon decrease the Cu extraction to less than 57.0% compared to 74.1% without additive, possibly due to the oxidation of these materials by oxygen under the test conditions. A more stable graphite powder was still easily oxidised resulting in a 20% drop in Cu extraction for 10 g/L graphite addition, as shown in Fig. 6. The lower copper extraction could be due to depleted oxygen available caused by extra reaction with added carbonaceous materials. Using a more inert Ti powder also resulted in a drop in Cu extraction from 74.1% to 64.8% when 2 g/L Ti powder was added. At higher additions, the Cu extraction starts to increase and produces a higher Cu recovery (of 87.1%) for 10 g/L addition of Ti powder. Either Ti powder was also oxidised and/or Ti in powder form did not provide adequate contact with the sulphide particles at these low levels (<10 g/L Ti), giving rise to the negative impact of Ti powder addition.
3.6 Mechanisms for pressure oxidation

Fig. 7 shows schematically the galvanic effect of chalcopyrite dissolution in the presence of a metal surface. The results of this study also strengthen the argument that the dissolution of copper sulphide minerals can be enhanced by the addition of pyrite forming a galvanic couple [22-24] and facilitating the transfer of electrons during the oxidation-reduction process. In this context several redox reactions (as shown in Fig. 7) can take place simultaneously and the Ti surface acts as a bridge for electrons to be transferred efficiently from one redox half-cell to another.

3.7 EDS Study of Feed and Leached Residues

Analysis of the feed and residues after the leaching shows the elemental mapping for S, O, Fe, Cu, Al and Si as major components of the materials tested.

The materials before and after leaching were generally very fine and only in agglomerates as shown where a full mapping can be detected. Fig. 8a shows the predominant distribution of these elements in agglomerates having size >20 microns. The mapping of S, Fe and Cu (bottom row) shows discrete grains for Fe/S and Cu/S most probably reflecting FeS₂ and CuS minerals (clear grains) and faint mapping of Cu/Fe/S as CuFeS₂. The mapping of O, Al and Si shows discrete grains of Si/O (quartz) and faint matrix of Al/Si/O most probably of albite and illite minerals. These results confirm the XRD results presented in Fig.1, showing major minerals of pyrite, chalcopyrite, chalcocite and gangue minerals of quartz, illite and albite.

After leaching the residues shows the disappearance of S. Some covellite (CuS) and pyrite (FeS₂) remains unreacted whereas most chalcopyrite grains disappear.

Figure 7. Galvanic couple enhancing the dissolution of chalcopyrite

Figure 8. EDS mapping of major elements of (a) feed and (b) residue (from experiment using teflon-lined reactor)

4. Conclusions

The pressure oxidation of chalcopyrite and other copper minerals is believed to take place via a redox reaction. The use of a Ti lining during the POX leaching of a low grade chalcopyrite concentrate yielded higher Cu recoveries at all conditions compared to when an inert teflonliner was used. Recoveries of > 90% could be achieved during POX leaching of a chalcopyrite/chalcocite concentrate at 200°C and 0.7 MPa initial oxygen pressure in 2 h. The slow heating did not seem to affect the Cu extraction greatly when a titanium lining is used by forming a galvanic couple that enhances the electro-oxidation of copper minerals. The oxidation of copper minerals and sulphur to sulphate at the anodic sites (mineral surface) encountered during POX leaching take place simultaneously with the reversible oxidation/reduction of the Fe³⁺/Fe²⁺ couple and oxygen reduction. The introduction of an electronic conductor, in this case the titanium surface, is indicated to enhance this redox process.

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References