LEACHING OF SECONDARY COPPER MINERALS USING REGENERATED FERRIC SULPHATE

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ABSTRACT

Secondary copper minerals such as chalcocite (Cu₂S) and covellite (CuS) are known to dissolve in acidic ferric sulphate solutions. However, the quantities of ferric sulphate required to achieve acceptable recoveries for high-grade copper feeds are prohibitive, unless the resulting ferrous sulphate is reoxidized and reused. A plant recently commissioned in Australia employs an autoclave for that purpose. This paper describes a novel approach, called the “Regenerated Ferric Sulphate Leaching (RFSL) process, in which the reoxidation of the ferrous ion is carried out under strictly atmospheric conditions, using SO₂/O₂ mixtures as the oxidizing medium. The process is very effective and rapid, and the reoxidation step can be accomplished during the leach itself or in a separate vessel. Several examples are presented for ores and concentrates originating from the USA, Central America and South East Asia. The overall concept of the process is also briefly assessed with respect to the main operating costs and sulfur balance.

INTRODUCTION

Chalcopyrite, CuFeS₂, is the most abundant copper sulphide mineral, and efficient treatment methods for producing high quality copper from chalcopyrite concentrates have been in use for several decades. The conventional treatment processes are pyrometallurgical and involve smelting, converting and electrefining. Hydrometallurgical processes have also been developed and are waiting for commercial recognition. Very recently, a demonstration plant to produce 30,000 T Cu/year has been built by Phelps Dodge in Bagdad (Arizona), and will make use of high temperature pressure oxidation to process chalcopyrite concentrates. Secondary copper sulphide minerals such as chalcocite (Cu₂S) or covellite (CuS), although not as abundant as chalcopyrite, represent a non-negligible source of copper. The enrichment zone of porphyry copper deposits (e.g. Morenci), or the sulphidic zones of Central African copper deposits, are examples of secondary copper minerals deposits.

Secondary copper minerals concentrates are also typically smelted either directly or after sulphate roasting. Secondary copper sulphide minerals are normally less refractory than chalcopyrite and as such appear more suitable to hydrometallurgical processes.

Acidified ferric sulphate is without a doubt the most common lixiviant for secondary copper minerals (1,2), and, even under autoclave conditions (3), it is believed that oxidation by ferric remains the most favoured mechanism. The dissolution reactions under atmospheric conditions can be written as follows for chalcocite and covellite, respectively:

\[
\begin{align*}
\text{Cu}_2\text{S} + 2 \text{Fe}_2(\text{SO}_4)_3 & \rightarrow 2 \text{CuSO}_4 + 4 \text{FeSO}_4 + \text{S}^0 \\
\text{CuS} + \text{Fe}_2(\text{SO}_4)_3 & \rightarrow \text{CuSO}_4 + 2 \text{FeSO}_4 + \text{S}^0
\end{align*}
\]

(1)

(2)

In the 1930’s already, it was recognized that the attack of chalcocite by ferric sulphate proceeded in two steps (4). The first step is fairly rapid and can overall be written as:

\[
\begin{align*}
\text{Cu}_2\text{S} + 2 \text{Fe}_2(\text{SO}_4)_3 & \rightarrow \text{Cu}_2\text{SO}_4 + 4 \text{FeSO}_4 + \text{CuS}
\end{align*}
\]

(3)

In fact, the reaction proceeds through the formation of a series of copper-deficient intermediates while cuprous ions diffuse through the solid to the surface, to be oxidized to cupric sulphate:

\[
\begin{align*}
\text{CuS} & \rightarrow \text{Cu}_{1.80-1.96} \text{S} \rightarrow \text{Cu}_{1.93-1.96} \text{S} \\
& \rightarrow \text{Cu}_{1.96} \text{S} \rightarrow \text{Cu}_{1.93} \text{S} \rightarrow \text{Cu}_{1.90} \text{S} \\
& \rightarrow \text{CuS}
\end{align*}
\]

(4)

The second step, that can be written as for the naturally occurring covellite, is much slower, due to the fact that reactants and reaction products must diffuse through a sulphur layer. The presence of ligands, most particularly chloride, has been shown to significantly improve the kinetics of the chalcocite dissolution, increasing the rate of the first step (through the formation of soluble copper species not requiring oxidation of CuI to CuII, for example CuCl₂) and of the second step (through the formation of a porous crystalline sulfur layer) (5,6,7,8).
Two moles of ferric iron are required to dissolve one mole of copper, and therefore, for the process to be practical, the ferric iron has to be regenerated. There are different means available to the metallurgist to regenerate the ferric iron.

- **Air or oxygen**: From a thermodynamic point of view, oxygen is an oxidant strong enough to oxidize ferrous iron, but the kinetics of the oxidation reaction are normally slow in the acid range.
- **Bacteria (for example thiobacillus ferrooxidans)**: Biological oxidation of ferrous iron is a well known process and is commonly applied in heaps to treat low grade secondary copper ores (9). Tank bio-oxidation has also been proposed for secondary copper concentrates (10,11,12).
- **Electro-oxidation**: Anodic oxidation of ferrous was already proposed by the Inspiration Consolidated Copper Corporation in the 1930’s (4).
- **Pressure oxidation**: Autoclaves have also been proposed as a means to oxidize ferrous iron, and under the higher temperatures and oxygen partial pressures involved, the reaction:

\[
2 \text{FeSO}_4 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}
\]  

is kinetically fast.

Examples of the use of autoclaves to reoxidize ferrous iron to attack secondary copper minerals are the Dynatec Las Cruces process (13,14,15,16), the Mount Gordon Gunpowder process (17), and the Copper Range in situ process.

- **SO_2/O_2 mixtures**: The oxidizing properties of SO_2/O_2 mixtures to oxidize ferrous iron have been known since the 1920’s work by the USBM. SO_2/O_2 mixtures have since been used to oxidize other ionic species such as CN- (Inco’s process), or manganese, or arsenic. Improved processes for Ni/Co-Mn and Zn-Mn separation (18) resulted from these studies. Based on all these studies, regenerated ferric sulphate leach processes were proposed for copper sulphide minerals and for zinc sulphide minerals, whereby SO_2/O_2 mixtures were used to regenerate ferric sulphate, either in-situ (during the leach) or ex-situ (in a separate reactor). Initial results have been presented for copper and zinc sulphide minerals (19,20).

**EXPERIMENTAL**

**DESCRIPTION OF THE SAMPLES TESTED**

Three samples were tested during this program; chemical and mineralogical analyses of these samples are presented in the following paragraphs. The first two samples were flotation concentrates, the first one produced during a pilot plant, the second one from a commercial operation in the South West USA. The last sample was an ore from a developing project.

Concentrate A was a flotation concentrate having pyrite as the main mineral and covellite as the major Cu-bearing mineral. A typical photomicrograph is presented in Figure 1. Concentrate B was also a flotation concentrate composed primarily of sulphides (94% weight), more particularly covellite (40% weight), chalcocite/digenite (18% weight) and pyrite (23% weight). A typical photomicrograph is presented in Figure 2. Concentrate C was an ore containing copper mostly as covellite, with minor chalcopyrite and enargite. The gangue was composed primarily of quartz and pyrite.
RESULTS

CONCENTRATE A

Ferric Sulphate Leach Results

The initial tests examined the response of the concentrate to acidified ferric sulphate additions. Results are summarized in Table II.

The results are not surprising; at high temperatures (80-90°C), provided that sufficient ferric is present, between 91 and 96% of the copper is extracted in 3-4 hours. However, the resultant leach solution (~41 g/L Fe, ~23 g/L Cu) would pose certain challenges to be addressed.

The application of SO₂/O₂ mixtures during the leach (to regenerate in-situ the ferric needed to extract the copper) allows similar good extractions (>95% Cu) to be achieved with only 10 g/L iron in solution, as indicated in Table III. Such leach solutions would be much easier to process.

The Use of SO₂/Air Mixtures

The results presented above confirm the suitability of SO₂/O₂ mixtures to regenerate the ferric iron needed to maintain copper extractions. In some areas, the cost of oxygen could be prohibitive, and, therefore, there could be significant economic incentives in using SO₂/Air mixtures. Several tests were conducted to examine whether SO₂/Air mixtures could be used to regenerate the ferric iron. The results are presented graphically in Figure 3.

If air alone was used instead of SO₂/Air (1.5% SO₂ v/v) mixtures, the copper extraction at 70°C after 6 hours would be 80.5% as compared with 96.7% when using 1.5% v/v SO₂ in the air.

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Table I: Chemical Analyses of the Samples Tested

<table>
<thead>
<tr>
<th>CONCENTRATE</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Caribbean</td>
<td>USA</td>
<td>Asia</td>
</tr>
<tr>
<td>%Cu</td>
<td>16.3</td>
<td>37.7</td>
<td>5.91</td>
</tr>
<tr>
<td>%Fe</td>
<td>24.1</td>
<td>17.1</td>
<td>11.2</td>
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<tr>
<td>%S²⁻</td>
<td>36.7</td>
<td>29.2</td>
<td>8.6</td>
</tr>
</tbody>
</table>

(10% solids; concentrate as received (P₈₀ = 17μm))

Table II - Summary Results of Ferric Sulphate Leach

<table>
<thead>
<tr>
<th>TEST #</th>
<th>TEMP (ºC)</th>
<th>DURATION (HRS)</th>
<th>INITIAL Fe³⁺ (g/L)</th>
<th>ACID ADDED (kg/t)</th>
<th>Cu EXTRACTED (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>3</td>
<td>10</td>
<td>305</td>
<td>56.3</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>3</td>
<td>40</td>
<td>305</td>
<td>90.9</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>4</td>
<td>40</td>
<td>305</td>
<td>96.1</td>
</tr>
</tbody>
</table>

(10% solids, 2% SO₂ (v/v))

Table III - Summary Results of Regenerated Ferric Sulphate Leach

<table>
<thead>
<tr>
<th>TEST #</th>
<th>TEMP (ºC)</th>
<th>DURATION (Hrs)</th>
<th>INITIAL Fe³⁺ (g/L)</th>
<th>ACID ADDED (kg/t)</th>
<th>SO₂/O₂</th>
<th>Cu EXTRACTED (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70</td>
<td>6</td>
<td>10</td>
<td>305</td>
<td>no</td>
<td>57.3</td>
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<tr>
<td>4</td>
<td>70</td>
<td>6</td>
<td>10</td>
<td>305</td>
<td>yes</td>
<td>68.7</td>
</tr>
<tr>
<td>5</td>
<td>70</td>
<td>6</td>
<td>10</td>
<td>305</td>
<td>yes</td>
<td>96.1</td>
</tr>
<tr>
<td>6</td>
<td>90</td>
<td>6</td>
<td>10</td>
<td>305</td>
<td>yes</td>
<td>98.3</td>
</tr>
</tbody>
</table>

Figure 3 - Effect of Temperature on the Kinetics of Cu Leaching Using Regenerated Ferric Sulphate (SO₂/Air mixtures) (10% solids; feed as-received: P₈₀ = 17μm)
CONCENTRATE B
The initial series of tests examined the suitability of SO₂/O₂ mixtures to regenerate ferric during the leach. The results are presented in Figure 4. Without regeneration, the best results that can be expected are 37.7% Cu dissolved, when all the ferric has been consumed. Adding oxygen during the leach promotes ferric regeneration, and, therefore, copper dissolution continues and achieves 62% in 6 hours under the conditions of the test. Adding SO₂ (2%) and replacing oxygen with air, while keeping the same flow of gases, produces the same copper extraction in 6 hours. Adding SO₂ to oxygen (5% SO₂ v/v), while keeping the same flow of gases, significantly improves the copper dissolution that reaches 88% in 6 hours. Clearly, SO₂/O₂ (or even SO₂/air) mixtures are more efficient than oxygen alone to regenerate ferric. The procedure is also quite reproducible (at the laboratory scale), as indicated in Figure 5. The effect of varying the proportion of SO₂ in the SO₂/O₂ mixture is presented in Figure 6.

The results indicate that 2% (v/v) SO₂ was sufficient to induce the maximum benefits of the gas blends. Higher percentages did not improve the results further, and there is some indication that 10% SO₂ in the blend had started reversing the benefits (too reducing conditions), at least initially.

As could be extrapolated from the shape of the dissolution curves, the dissolution was not completed in 6 hours, and longer retention times would increase the copper yield. This was confirmed as illustrated in Figure 7.

As expected for the dissolution of copper from covellite when using acidified ferric sulphate, the rate-limiting step is the migration of reactants and/or reaction products through the sulfur layer. This was confirmed by the linear correlation (at least at the beginning) of the type: g/L Cu dissolved = k √T, as illustrated in Figure 8.

CONCENTRATE C
Initial tests were carried out to confirm the beneficial effect of SO₂/O₂ mixtures to improve the regeneration of ferric during the leach (Figure 9). The results confirmed the beneficial effect of SO₂/O₂ mixtures for the regeneration of ferric and the improvement on copper dissolution. Without in-situ regeneration, 30 g/L Fe³⁺ must be added to achieve acceptable copper extraction (~95% in 4 hours). With ferric regeneration (using SO₂/O₂ mixtures with 2% SO₂), the required ferric concentrate concentration could be reduced to 10, 5 and even 2 g/L to achieve similar extractions. Oxygen alone is not as efficient to regenerate ferric as illustrated in Figure 10.
Comparing the results of various tests, one can easily see that the addition of small amounts of SO₂ to the oxygen (same flowrate) resulted in a largely improved ferric regeneration, with 88% of the copper dissolved in 60 minutes compared to 80% in 120 minutes when pure oxygen was used. With slightly higher ferric (5 g/L), SO₂/O₂ mixtures led to 93% Cu dissolution in only 60 minutes.

**DISCUSSION**

The results presented here on three samples (containing chalcocite or covellite minerals primarily as copper-bearing minerals) certainly confirmed the results presented earlier, namely that SO₂/O₂ mixtures are a very effective oxidant to regenerate ferric sulphate solutions. All the results presented here deal with the in-situ regeneration of ferric sulphate (i.e. the regeneration of ferric sulphate is accomplished in the leach reaction vessel while copper sulphide minerals are being attacked), but earlier results indicated that the regeneration could easily be accomplished on solutions ex-situ in a separate vessel.

Examination of the mechanism(s) of ferric sulphate dissolution of chalcocite and covellite was not the primary objective of this work, since that issue had been tackled by numerous researchers.

To understand the reason for such an improvement in the efficiency of copper dissolution when regenerating ferric sulphate with SO₂/O₂ mixtures, one has to examine what part of the reaction path necessitates high ferric concentrations.

According to a 1974 review (1), the rate-limiting step for chalcocite dissolution when using acidified ferric sulphate is the diffusion in solid solution of ferric ions to the Cu₂S surface; at the surface of the chalcocite, the oxidation by ferric of Cu(I) migrated from the inner mineral must therefore occur rapidly; when all the mineral chalcocite has been transformed to blue-remaining covellite ('blaubleibender'), ferric has to diffuse through the sulfur layer to the inner mineral, while ferrous sulphate and copper sulphate have to diffuse through the same sulfur layer to the outer mineral. The relatively low activation energies measured by several authors (1.5 to 7 Kcal/mole, 6 to 18 kJ/mole) indicate that the sulfur layer produced from 'blaubleibender' must be quite porous and does not constitute a high barrier to the progress of the reaction. It can therefore be postulated that the contribution of SO₂/O₂ mixtures to the improved kinetics of chalcocite dissolution is to maintain a higher concentration of ferric in solution, thereby favouring Fe³⁺ diffusion because of the concentration gradient.

The same reviewer for covellite dissolution using acidified ferric sulphate solution concluded to a chemically controlled process, with a significantly higher activation energy (8-25 kcal/mol, 32-100 kJ/mole). Some results presented here point to a mechanism controlled by diffusion through a reaction product when using a SO₂/air mixture. Additional work would be required to fully understand the reaction mechanism.
A rate expression for the oxidation of ferrous solution when using \( \text{SO}_2/\text{O}_2 \) mixtures has been presented in earlier publications and can be summarised as:

\[
d\text{Fe}^{2+}/dt = k' \left[ \text{SO}_2 \right]^a \left[ \text{SO}_3 \right]^b \exp \left( -\frac{E}{RT} \right)
\]

(6)

where \( a, b \) and \( c \) are 2.1, 1.1 and 2.5 respectively, and \( E \) equals 6,650 J/mole and \( k' = k'' [pO_2] \).

It is unquestionable that the \( \text{SO}_2/\text{O}_2 \) mixtures enhance the kinetics of ferric sulphate leaching of chalcocite and covellite ores or concentrates. To assess the industrial applicability of a new process, one cannot stop to that consideration and must also consider the implications of introducing \( \text{SO}_2 \) on the overall process sulfur balance.

The first point to consider is that little pyrite is attacked by ferric sulphate, and therefore, sulphate ions introduced by the oxidation of pyrite are a minor contributor to the overall solution sulphate balance. Moreover, there is no evidence that pyrite oxidation by ferric sulphate is increased when adding \( \text{SO}_2/\text{O}_2 \) mixtures.

If one examines the overall sulphate balance of the whole process, including leaching, ferric regeneration, solvent extraction and copper electrowinning when using oxygen alone or \( \text{SO}_2/\text{O}_2 \) mixtures, one arrives at the following reactions:

a) For Chalcocite

With oxygen:

\[
\begin{align*}
\text{Cu}_2\text{S} + 2\text{Fe}_2(\text{SO}_4)_3 & \rightarrow 2\text{CuSO}_4 + 4\text{FeSO}_4 + \text{S}_0 \quad \text{(L)} \\
4\text{FeSO}_4 + \text{O}_2 + 2\text{H}_2\text{SO}_4 & \rightarrow 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \quad \text{(R)} \\
2\text{CuSO}_4 + 2\text{H}_2\text{O} & \rightarrow 2\text{Cu}^{\oplus} + \text{O}_2 \uparrow + 2\text{H}_2\text{SO}_4 \quad \text{(EW)} \\
\text{Cu}^{\oplus} + \text{O}_2 & \rightarrow 2\text{Cuo} + \text{O}_2 \uparrow + \text{S}_0 \quad \text{(overall)}
\end{align*}
\]

With \( \text{SO}_2/\text{O}_2 \) :

\[
\begin{align*}
\text{Cu}_2\text{S} + 2\text{Fe}_2(\text{SO}_4)_3 & \rightarrow 2\text{CuSO}_4 + 4\text{FeSO}_4 + \text{S}_0 \quad \text{(L)} \\
4\text{FeSO}_4 + 2\text{SO}_2 + 2\text{O}_2 & \rightarrow 2\text{Fe}_2(\text{SO}_4)_3 \quad \text{(R)} \\
2\text{CuSO}_4 + 2\text{H}_2\text{O} & \rightarrow 2\text{Cu}^{\oplus} + \text{O}_2 \uparrow + 2\text{H}_2\text{SO}_4 \quad \text{(EW)} \\
\text{Cu}_2\text{S} + 2\text{SO}_2 + 2\text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 2\text{Cu}^{\oplus} + \text{O}_2 \uparrow + 2\text{H}_2\text{SO}_4 + \text{S}_0 \quad \text{(overall)}
\end{align*}
\]

b) For Covellite

With oxygen:

\[
\begin{align*}
\text{CuS} + \text{Fe}_2(\text{SO}_4)_3 & \rightarrow \text{CuSO}_4 + 2\text{FeSO}_4 + \text{S}_0 \quad \text{(L)} \\
2\text{FeSO}_4 + 1\text{O}_2 + \text{H}_2\text{SO}_4 & \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \quad \text{(R)} \\
\text{CuSO}_4 + \text{H}_2\text{O} & \rightarrow \text{Cuo} + \text{H}_2\text{SO}_4 + \frac{1}{2}\text{O}_2 \uparrow \quad \text{(EW)} \\
\text{CuS} + \frac{1}{2}\text{O}_2 & \rightarrow \text{Cuo} + \frac{1}{2}\text{O}_2 \uparrow + \text{S}_0 \quad \text{(overall)}
\end{align*}
\]
With $SO_2/O_2$:  
\[
\begin{align*}
CuS + Fe_2(SO_4)_3 & \rightarrow CuSO_4 + 2FeSO_4 + S^0 \\
2FeSO_4 + SO_2 + O_2 & \rightarrow Fe_2(SO_4)_3 \quad (L) \\
CuSO_4 + H_2O & \rightarrow CuO + \frac{1}{2}O_2 \uparrow + H_2SO_4 \quad (EW)
\end{align*}
\]

L, R, EW represent the leaching, regeneration and the electrowinning stages, respectively.

Based on the overall reactions, when using $SO_2/O_2$ mixtures, the theoretical results presented here indicate that $SO_2$ could be used instead of pure oxygen; however, the kinetics would be slower with oxygen alone.

The equipment to be used consists of conventional and simple tanks, mixers, pumps, thickeners/filters, gas spargers; since no chloride is used in the process, corrosion is not a significant issue.

Regarding operating costs, it is not possible to give a figure because each case will be different, depending on the concentrate to be treated, its acid-consuming components, the availability of cheap limestone or a source of oxide copper to consume excess acid (oxide copper concentrate, heap leach operations).

To be able to match the composition of the resulting PLS to the requirement of conventional solvent extraction circuits, the copper tenor has to be adjusted to less than about 20 g/L, and therefore, the percent solids in the leach circuit has to be adjusted accordingly. In practice, this indicates that the process is better suited to high grade ores or low grade concentrates (for example 10-15% Cu). This brings an additional benefit from this process since it allows the mineral processor to increase the overall copper yield by producing a lower grade concentrate, for example a rougher or a first cleaner concentrate.

**REFERENCES**


