COPPER ARSENIDE MINERALS AS A SUSTAINABLE FEEDSTOCK FOR THE COPPER INDUSTRY

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ABSTRACT

Copper arsenide minerals, such as enargite (Cu₃AsS₄), can be processed by pyrometallurgical techniques, e.g. roasting followed by smelting. Such processes, however, may not be sustainable in the long run due to the decreasing market for the resulting arsenic trioxide dust. Hydrometallurgical processes are being proposed to treat copper sulphide feeds, and these can be readily adapted to treat copper arsenide minerals. A brief review of the hydrometallurgical treatment options for copper arsenide minerals is presented. The most promising route to treat copper arsenide minerals is the High Temperature Pressure Oxidation Process (HTPOX) which, in addition to extracting the copper, fixes the arsenic as scorodite, an arsenic product that is stable, according to the USEPA TCLP leachate test. Several examples of the laboratory application of pressure oxidation for various copper arsenide feeds are provided, and the discussion is focused on the fate and the stability of the arsenic in the various streams of the process.

INTRODUCTION

Chalcopyrite CuFeS₂ is the most common copper sulphide mineral, and as such, contributes to the majority of the world copper production. There are other copper sulphide minerals contributing a significant portion of copper production, such as bornite Cu₄FeS₄, chalcocite Cu₃S, covellite CuS. There are also large deposits containing copper arsenide minerals, primarily enargite Cu₃AsS₄ and tennantite Cu₄AsS₄S₁₃.

This paper reviews the processing alternatives available to the metallurgist to recover copper from copper arsenides. The focus is placed on the various hydrometallurgical treatment processes developed for enargite ores or concentrates, with a special emphasis on the fate of arsenic during the treatment. A most promising route appears to be the high temperature pressure oxidation (HTPOX) process, which allows for an almost complete dissolution of the copper, while at the same time, under the proper conditions, to the stabilization of most of the arsenic as scorodite (FeAsO₄·2H₂O). The remaining of the arsenic might be stabilized as scorodite, even under atmospheric conditions.
HYDROMETALLURGICAL TREATMENTS

These could be classified in two main categories: Processes aiming at removing the arsenic, leaving behind a saleable copper concentrate suitable for the conventional market; and secondly, processes aiming at solubilizing the copper and somehow generating a stable arsenic residue.

De-Arsenification of Copper Arsenides

Alkaline leaching of copper arsenides, using Na₂S (or NaOH + NaSH = Na₂S + H₂O) is a well known process (5) and it produces a copper concentrate (Cu₂S) suitable for sale. The process is largely based on the Sunshine Mining process, used commercially for many years for a tetrahedrite concentrate (6).

The reactions for enargite and tennantite are as follows:

\[ 2 \text{CuAsS}_4 + 3 \text{Na}_2\text{S} \rightarrow 2 \text{Na}_3\text{AsS}_4 + 3 \text{CuS} \]  
\[ 3 \text{Cu}_2\text{SAsS}_3 + 3 \text{Na}_2\text{S} \rightarrow 2 \text{Na}_3\text{AsS}_4 + 3 \text{CuS} \]  

(1)  

(2)

Equity Silver operated a commercial plant for several years based on this process and treating a tetrahedrite-tennantite concentrate assaying 17.3% Cu, 23.5% Fe, 4.1% As, 7.1% Sb and 6800 g/t Ag (78). The clean concentrate target was 22.25% Cu, 0.3% Sb and 15% As. The residual arsenic originated from some arsenopyrite, FeAsS, that remained inert under the leach conditions. During the process, antimony was removed as sodium antimonate [NaSb(OH)₃] for sale, while arsenic was crystallized as calcium arsenate Ca₃(AsO₄)₂ that had to be disposed in a permanent impoundment.

Caustic leaching of copper arsenides also appeared as a suitable candidate to selectively dissolve the arsenic based on the success of a similar process as applied to cobalt arsenides from Cobalt, Ontario (The Sill process). However, the process was tested at the bench scale on an enargite concentrate from the Lepanto Mine in the Philippines without success (9).

Copper Dissolution Processes

A. Atmospheric processes

A.1 Acidic oxidizing processes

Previous research (10) has indicated that the oxidation of enargite, in the presence of oxygen, occurs in two stages:

\[ 4 \text{Cu}_3\text{AsS}_4 + 3\text{O}_2 \rightarrow 12 \text{CuS} + 2 \text{As}_2\text{O}_3 + 4\text{S} \]  
\[ \text{CuS} + 2\text{O}_2 \rightarrow \text{CuSO}_4 \]  

(3)  

(4)

The overall reaction is fairly slow, and even after milling for 10 hours in oxygen and leaching for 24 hours in 0.5 M HCl, only 36.6% of the enargite had been dissolved (11). In the presence of ferric sulphate, other investigators (12) found that the overall reaction was:

\[ \text{Cu}_3\text{AsS}_4 + 17.5\text{Fe}_3^++ 9\text{H}_2\text{O} \rightarrow 3 \text{Cu}^{2+} + 2\text{O}_2 + 2\text{As}_2\text{O}_3 + 36\text{Fe}^{2+} + 12.75\text{SO}_4^{2-} + 18\text{H}^+ + 17.5\text{Fe}^{3+} \]  

(5)

The investigators found that dissolution kinetics were linear, and interpreted it as a reaction controlled by a surface reaction. As a whole, the dissolution kinetics were slow. The same authors investigated also the dissolution of tennantite with acidic ferric chloride (13), and found that the reaction to proceed as per:

\[ \text{Cu}_2\text{SAsS}_3 + 36\text{Fe}^{3+} + 12\text{H}_2\text{O} \rightarrow 12 \text{Cu}^{2+} + 4\text{H}_3\text{AsO}_3 + 36\text{Fe}^{2+} + 13\text{S}^{2-} + 12\text{H}^+ \]  

(6)

with the process being chemically or electrochemically controlled.

A.2 Bacterial processes

Bacterial oxidation has been examined by several authors (11), but it has shown so far little promise with only 11% of the copper dissolved after 700 hours, as compared with 4.5% Cu after 550 hours in the absence of bacteria.

B. Pressure leaching processes

B.1 Ammonia pressure leaching

Ammonia leaching was applied to enargite at small oxygen overpressures (14). The reaction involved can be written as:

\[ \text{Cu}_3\text{AsS}_4 + 13\text{NH}_4^+ + 8.75\text{O}_2 + 2.5\text{H}_2\text{O} \rightarrow 3 \text{Cu}[^{2+}] + ^{2+} + \text{NH}_4\text{H}_2\text{AsO}_4 + 4\text{SO}_4^{2-} + 2\text{H}^+ \]  

(7)

The transfer rate of copper and arsenic to solution was rather slow, and only 80% of the copper was extracted under the experimental conditions.

B.2 Acidic pressure leach

Commercial application of continuous autoclaves for the oxidizing pressure leaching of metal sulphides was made possible in the early 1950’s thanks to the pioneering work of the Chemical Construction Company (a subsidiary of American Cyanamid) and Sherritt Gordon Mines Limited (15). The very first commercial plants did in fact process cobalt arsenides (16).

The great success enjoyed by the process for treating refractory gold ores, sphalerite concentrates, and Cu/ Ni mattes has shown the potential to apply the process for other Ni/Co feedstocks (17), cobalt arsenides (18) and chalcopyrite concentrates (19).

More particularly for copper arsenides, enargite concentrates from the Lepanto Mine in the Philippines were treated in a batch autoclave at 225°C and 150 psi oxygen overpressure (9). Up to 98% Cu was dissolved when pyrite was blended to the enargite and arsenic was precipitated as ferric arsenate. Without pyrite additions, copper dissolutions were well below 70%.

In 1993, high temperature pressure oxidation (HTPOX) was recommended by SGS Lakefield to process El Indio enargite concentrate, since it would allow, under the best conditions, to recover most of the copper (98-99%) on site as copper metal, would stabilize arsenic (and antimony) in the residue as scorodite, and would allow gold/silver recovery from the residue using conventional cyanidation (20). Similarly, in 1994, SGS Lakefield developed at the bench scale, a high temperature pressure oxidation process to treat Codelco chalcocite-enargite concentrate (21).
Benchtop HTPOX results for the El Indio enargite whole ore and concentrate were presented by UBC investigators in 1999 (22). The concentrate assayed 22.6% Cu, 18.0% Fe, 35.4% S and 8.6% As. HTPOX temperature varied between 200-220°C, and retention time between 60 and 180 minutes. Sulphide oxidation was near complete, but copper extraction was only 95%. It was attributed to copper re-precipitation as a mixed Fe-Cu-As-S-O compound. On the whole ore, assaying 2.54% Cu, 9.52% Fe, 11.3% S and 0.93% As, HTPOX at 25% solids, 220°C, gave 99.4% Cu extraction in 60 minutes, producing a PLS assaying 8.6 g/L Cu, 4.9 g/L Fe, 49 g/L H₂SO₄ and 0.5 g/L As.

Over the years, SGS Lakefield has conducted several bench scale and pilot plant studies on various cobalt, nickel and copper arsenides. The results of HTPOX tests on various enargite concentrates are presented in Table I. Feeds to the HTPOX were all flotation concentrates, some rougher concentrates, other cleaner concentrates. All the concentrates were tested as-received, without further regrinding.

The copper extractions produced on the cleaner concentrate assaying 30.7% Cu were relatively low at 95%, leaving a residue at ~4.4% Cu. These results are similar to those obtained by UBC investigators on El Indio concentrate. US EPA TCLP 1311 procedure applied on the HTPOX residue indicated it was stable (<5 mg/L As in leachate). Mineralogical examination of the residue indicated it was mostly Type 2 Iron Arsenate, with minor presence of Type I Iron Arsenate with copper.

For all other concentrates, copper extractions from the enargite or enargite/chalcopyrite rougher concentrates were excellent (>99%), with the majority of the arsenic reporting to the residue as a stable compound (as measured by the TCLP procedure).

When treating a copper concentrate (enargite), solutions containing high levels of Cu, As and Fe are produced, and although scorodite (or Type 2 compound) precipitation is preferred, it is suggested that there is also a certain extent of precipitation of an Fe-As-Cu-S compound, leading to copper losses in the residue. When treating a lower grade enargite concentrate (rougher) or an enargite-containing ore, the solution levels of Cu, As, Fe are much lower and the Fe-As-Cu-S compound does not precipitate to any measurable extent, resulting in very high copper extractions.

### Table I – Summary of HTPOX Results on Various Enargite Concentrates

<table>
<thead>
<tr>
<th></th>
<th>CHILE Ro Conc</th>
<th>PERU Ci Conc</th>
<th>PERU Ci Conc</th>
<th>S. AMERICA Ci Conc</th>
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<td>T-2</td>
<td>T-3</td>
<td>T-4</td>
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<tr>
<td>% Cu</td>
<td>6.56</td>
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<td>% As</td>
<td>0.72</td>
<td>0.13</td>
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<td>% Fe</td>
<td>5.74</td>
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<tr>
<td>% S</td>
<td>12.3</td>
<td>18.3</td>
<td>30.5</td>
<td>28.2</td>
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<td>HTPOX conditions</td>
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<td>Temp °C</td>
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<td>psi O₂</td>
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<td>g/L NaCl</td>
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<td>-</td>
<td>20</td>
<td>-</td>
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<td>Results</td>
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<tr>
<td>% Cu Extraction</td>
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<td>99.0</td>
<td>99.5</td>
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<tr>
<td>% As Extraction</td>
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<td>37.0</td>
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<tr>
<td>g/L Cu</td>
<td>7.0</td>
<td>8.49</td>
<td>12.0</td>
<td>33.0</td>
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<tr>
<td>g/L As</td>
<td>0.16</td>
<td>0.007</td>
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<td>0.086</td>
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<tr>
<td>g/L Fe</td>
<td>0.14</td>
<td>0.28</td>
<td>4.6</td>
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<tr>
<td>Residue Assays</td>
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<tr>
<td>% Cu</td>
<td>0.07</td>
<td>0.04</td>
<td>0.15</td>
<td>0.25</td>
</tr>
<tr>
<td>% As</td>
<td>0.67</td>
<td>0.16</td>
<td>5.20</td>
<td>1.24</td>
</tr>
</tbody>
</table>

### Precious Metals Recovery from the HTPOX Residue

Copper arsenides are often associated with precious metals (gold and silver), and any process to treat copper arsenides must be able to handle and recover their precious metals content.

#### Gold Recovery

As was the case of using HTPOX for chalcopyrite-gold concentrates (23), gold recovery from the residue of HTPOX applied to enargite concentrates is relatively straightforward: assuming cyanidation is not under a regulatory ban, it will recover most of the gold with minimum cyanide consumption, since there is practically no elemental sulfur in the residue.

Residue from test T-2 in Table I was submitted to a standard cyanidation: 92% of the gold was recovered from the residue assaying only 0.25 g/t Au, with a cyanide consumption of 3.3 kg NaCN/T concentrate. Gold extraction by cyanidation was also shown to be straightforward from HTPOX residues by the UBC investigators, with the exception of high lime consumption.

As an alternative to cyanide, the PLATSOL process (basically HTPOX conditions with the addition of 5-10 g/L NaCl, reference (24)) has also been proposed to dissolve copper and gold in the autoclave, and it can also be applied...
to enargite gold feeds. Test T-3 was conducted under PLATSOL conditions (Table I), and 95% of the Au was dissolved in the autoclave, together with copper, from a concentrate assaying 50 g/t Au.

Silver Recovery
Under typical HTPOX conditions, silver in the autoclave forms argento-jarosite which does not respond to cyanidation, unless a lime boil pretreatment step is applied (22). Under PLATSOL conditions, it has been shown that silver chloride AgCl forms preferentially to silver jarosite. AgCl in the residue responds very well to cyanidation. Alternatively, if cyanide usage is not acceptable, AgCl will respond well to thiosulphate leaching (25).

The Recovery of Copper from HTPOX Liquors
The liquor from the HTPOX treatment of enargite concentrates contains principally Cu, As, Fe and free acid. It would be very convenient to feed that liquor to a conventional copper solvent extraction circuit, and in most cases, this will imply having to neutralize some of the excess acid up to a pH of about 2.0. If an acid sink is not readily available, such as a heap or a copper oxide concentrate, or carbonate tailings, limestone will have to be added. Extreme care must be taken during this step to avoid overshooting the pH and precipitating unstable calcium arsenates/arsenites compounds. Once the excess acid has been neutralized, the liquor can be treated in a conventional Cu SX circuit. Table II presents the results of laboratory mixer settler treatment of a Cu-As solution.

As expected, using conventional extractants, copper was selectively extracted from the copper-arsenic leach liquor.

Stabilization of the Arsenic During HTPOX
A large proportion of the arsenic is precipitated during HTPOX as scorodite FeAsO$_4$·2H$_2$O or Type 2 compound (26) under the proper experimental conditions. Both compounds are very stable as measured by the US EPA TCLP test. Figure 1 presents a micrograph of scorodite crystals precipitated at SGS Lakefield at 170°C, and in equilibrium with a solution containing 15 g/L Cu, 0.9 g/L As, and 30 g/L H$_2$SO$_4$. Higher temperatures in the autoclave normally produce Type 2 compound (under the proper Fe/As ratios) (27).

However, the PLS coming out of the autoclave still contains too high levels of As for the SX barren to be allowed to be discarded. That arsenic in the PLS must therefore be stabilized. Two options are available: stabilize the As after copper solvent extraction, or prior to it.

A. Stabilizing the As in the PLS after Cu SX

The results presented earlier confirmed that copper can be selectively extracted from the neutralized PLS. After Cu SX, arsenic can be precipitated from the solution and the most common process is precipitation as ferric arsenate after proper adjustment of the Fe$_3$+/As$_5$+ under ratio (>3/1). This procedure is fairly common in industry.

B. Stabilizing the As in the PLS prior to Cu SX

Researchers at McGill University in Montreal have developed an atmospheric pressure process to precipitate crystalline scorodite from various effluents (28). Under controlled conditions (temperature >90°C, seed recycle, controlled addition of lime to slowly raise the pH), crystalline scorodite could be precipitated from sulphate and chloride solutions, at a pH around 1.0, using an Fe/As molar ratio of ~1. Figure 2 presents a micrograph of scorodite precipitated at atmospheric pressure during a recent test program at SGS Lakefield.

The picture clearly shows the scorodite and the gypsum crystals; no calcium arsenates/arsenites were detected and this was confirmed by the US EPA TCLP results, which indicated that the residue was stable. Little data have been published on the application of McGill scorodite process on solutions containing high copper tenors; very preliminary indication is that scorodite forms preferentially to Cu-As compounds, but more work is needed in this area.

**PROPOSED FLOWSHEET**

Based on the information available to date, the following flowsheet is proposed to treat copper arsenide concentrates (Figure 3). The proposed flowsheet is identical to HTPOX when applied to chalcocite concentrates. Once evidence has been gathered that the atmospheric scorodite precipitation is not affected by the presence of high tenors of Cu, it could be introduced prior to Cu SX and would result in savings in ferric sulphate additions.

<table>
<thead>
<tr>
<th>STREAM</th>
<th>Cu, g/L</th>
<th>As, g/L</th>
<th>Cu/As RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLS</td>
<td>0.044</td>
<td>3.98</td>
<td>0.022</td>
</tr>
<tr>
<td>Barren</td>
<td>11.7</td>
<td>0.086</td>
<td>266</td>
</tr>
<tr>
<td>Strip solution</td>
<td>20</td>
<td>3.8</td>
<td>5.3</td>
</tr>
</tbody>
</table>

Table II – Cu SX from a Cu/As Leach Liquor Organic = 20% LIX 984 in Isopar M; O/A = 3/1; contact time = 5 minutes; pH = 1.9; temp = 40°C; strip sol'n = 200 g/L H$_2$SO$_4$"
extractants; the arsenic left in the raffinate can then be rejected as stable ferric arsenate. Copper extractions from high grade copper-arsenic concentrates are limited to about 95%, due to reprecipitation of a Fe-As-Cu-S-O compound.

REFERENCES


CONCLUSIONS

Pyrometallurgical treatment of copper arsenide concentrates has been commercially practiced but that route might no longer be acceptable because of the increasingly poor marketability of the arsenic trioxide by-product.

The hydrometallurgical treatment of copper arsenides can take two forms. Arsenic can be dissolved selectively from the arsenide with Na₂S, leaving behind a copper concentrate (Cu₂S) acceptable for the market. The dissolved arsenic can be crystallized as sodium thioarsenate, for example, and then converted to arsenic sulphide for disposal in a contained area.

The second option consists in submitting the copper arsenide concentrate to high temperature pressure oxidation. From low grade concentrates, more than 99% of the copper is dissolved, while most of the arsenic is stabilized in the residue as scorodite or Type 2 compound. Copper can be selectively extracted from the PLS using conventional organic

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**Figure 3** – Flowsheet Proposed to Treat Copper Arsenide Minerals

Finally, it should be mentioned that there is increasing evidence that arsenic residues could become destabilized if disposed under reducing conditions (29). Reducing conditions could originate from mixing the arsenic residues with other products containing sulphide minerals; it could also originate from organic compounds generated by bacterial activity.

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21. C.J. Ferron, Personal communication to Codelco Scientific Council, La Serena, Chile, April 1995


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