Arsenic: The Argument for Hydrometallurgical Processing and Stabilization at the Mine Site

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Introduction

• Why Arsenic?
  • Arsenic often occurs as an impurity in ores and concentrates.
  • Availability of “clean” ores and concentrates is declining – need to treat materials with high arsenic levels.
  • Copper concentrates widely traded - The occurrence of arsenic in copper concentrates is a major target for effective treatment.

• Why Hydrometallurgy
  • Hydrometallurgical technologies for arsenic fixation or extraction of metals from arsenical resources are effective.
  • First, hydrometallurgy avoids the high temperatures inherent in smelting processes and therefore limits the possibility of generation of arsenic dusts and gases.
  • Second, hydrometallurgy can selectively remove metals from an arsenical concentrate without mobilizing the arsenic at the same time.
Thermodynamic Considerations

- Arsenic occurs with oxidation states of (+5, +3, 0 and -3).
- The +5 and +3 oxidation state (arsenate and arsenite) species are soluble right across the whole pH range.
- Elemental arsenic also occurs across the entire pH range and arsine (AsH₃(g)) occurs under very reducing conditions across the pH range.
- Arsenic can therefore be viewed as very mobile in a water-based system.
- The method of reducing mobility of arsenic involves precipitation of arsenic.
- The preferred method of precipitation is as ferric arsenate or a ferric co-precipitate.
The As-H₂O Eh-pH Diagram at 25 °C with 0.1 mol/kg H₂O As Species. (Outotec HSC Version 7.1)
Treatment of Copper Concentrates

• The treatment of copper concentrates by smelting – converting and electrorefining has dominated the copper industry since the 1800’s.

• Research and development in searching for hydrometallurgical alternatives to traditional pyrometallurgy processes has intensified in recent years.

• A whole range of chemical and biological processes for copper recovery from concentrates have emerged.

• These processes are all successful in (1) dissolving copper from concentrates, (2) purifying the leach solutions using modern separation processes and (3) recovering a high value, high purity copper metal product.

• The main target of the historical and current developments has been concentrates containing chalcopyrite minerals.

• Less effort has been applied to solving the problem on enargite-containing concentrates.
## World Copper Concentrate Survey

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cu</th>
<th>Sb</th>
<th>As</th>
<th>Zn</th>
<th>Pb</th>
<th>Ni</th>
<th>Ag</th>
<th>Cd</th>
<th>Co</th>
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<tbody>
<tr>
<td>$P_{0%}$</td>
<td>14.0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
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<tr>
<td>$P_{50%}$</td>
<td>26.7</td>
<td>0.010</td>
<td>0.110</td>
<td>0.620</td>
<td>0.140</td>
<td>0.002</td>
<td>0.006</td>
<td>0.004</td>
<td>0.005</td>
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<tr>
<td>$P_{60%}$</td>
<td>27.6</td>
<td>0.015</td>
<td>0.139</td>
<td>1.31</td>
<td>0.266</td>
<td>0.004</td>
<td>0.008</td>
<td>0.006</td>
<td>0.009</td>
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<tr>
<td>$P_{70%}$</td>
<td>28.5</td>
<td>0.022</td>
<td>0.180</td>
<td>2.87</td>
<td>0.562</td>
<td>0.008</td>
<td>0.011</td>
<td>0.010</td>
<td>0.013</td>
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<tr>
<td>$P_{80%}$</td>
<td>30.0</td>
<td>0.042</td>
<td>0.272</td>
<td>3.65</td>
<td>1.48</td>
<td>0.010</td>
<td>0.017</td>
<td>0.014</td>
<td>0.024</td>
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<tr>
<td>$P_{90%}$</td>
<td>34.0</td>
<td>0.102</td>
<td>0.410</td>
<td>5.63</td>
<td>2.91</td>
<td>0.024</td>
<td>0.068</td>
<td>0.026</td>
<td>0.040</td>
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<tr>
<td>$P_{100%}$</td>
<td>51.1</td>
<td>7.25</td>
<td>7.50</td>
<td>9.28</td>
<td>12.7</td>
<td>1.03</td>
<td>1.91</td>
<td>0.072</td>
<td>0.250</td>
</tr>
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</table>

Simplified Flowsheet

Copper Ore or Concentrate → Copper Leaching

As? → Reagents

Copper Leaching → S/L Separation

Wash Water → S/L Separation

Raffinate → Copper SX-EW

As? → Copper SX-EW

Copper SX-EW → Copper Cathode

As? → Copper Cathode

S/L Separation → Precious Metal Recovery

Gold and Silver → Precious Metal Recovery

As? → Precious Metal Recovery

Precious Metal Recovery → Final Residue

As? → Final Residue
## Current Copper Leach Process Options (Sulfate)

<table>
<thead>
<tr>
<th>Process</th>
<th>Status</th>
<th>Temp. (°C)</th>
<th>Press. (atm)</th>
<th>Ultrafine Grind</th>
<th>Chloride</th>
<th>Surfactant</th>
<th>Special</th>
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<tbody>
<tr>
<td>Activox Process</td>
<td>D</td>
<td>110</td>
<td>12</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
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<tr>
<td>Albion Process</td>
<td>P</td>
<td>85</td>
<td>1</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
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<tr>
<td>AAC-UBC</td>
<td>P/C</td>
<td>150</td>
<td>12</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td></td>
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<tr>
<td>Bactech/Mintek Low T Bioleach</td>
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<td>35</td>
<td>1</td>
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<td>No</td>
<td>No</td>
<td></td>
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<tr>
<td>BIOCOP™</td>
<td>C</td>
<td>80</td>
<td>1</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Thermo-philic</td>
</tr>
<tr>
<td>CESL Process</td>
<td>C</td>
<td>150</td>
<td>12</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Cobre Las Cruces</td>
<td>C</td>
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<td>1</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Chalcocite</td>
</tr>
<tr>
<td>Dynatec</td>
<td>P</td>
<td>150</td>
<td>12</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Coal + Recycle</td>
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<tr>
<td>FLSMIDTH</td>
<td>B</td>
<td>85</td>
<td>1</td>
<td>No/Yes</td>
<td>No</td>
<td>No</td>
<td>Pre-activation/Intrastage grind</td>
</tr>
<tr>
<td>Galvanox</td>
<td>P</td>
<td>80</td>
<td>1</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Galvanic</td>
</tr>
<tr>
<td>Mt. Gordon</td>
<td>C</td>
<td>90</td>
<td>8</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Chalcocite</td>
</tr>
<tr>
<td>PLATSOL</td>
<td>P</td>
<td>225</td>
<td>32</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td></td>
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<tr>
<td>Sepon Copper</td>
<td>C</td>
<td>80 – Cu</td>
<td>1</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Chalcocite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220 – FeS₂</td>
<td>32</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Total Press. Ox.</td>
<td>C</td>
<td>225</td>
<td>32</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
</tbody>
</table>
Copper Concentrate Treatment: Leading Candidates for High Arsenic Concentrates

- BIOCOP™
- GALVANOX™
- Total Pressure Oxidation (TPOX)/PLATSOL™
- CESL Process
- Rapid Oxidative Leach (ROL™)
- Alkaline Sulfide Leaching (ASL)
GALVANOX™ PROCESS

• Process developed by David Dixon with Alain Tshilombo and Ghazaleh Nazari

• Atmospheric leaching of chalcopyrite

• \( \sim 80 \, ^\circ \text{C} \), no bacteria, no chloride, no surfactants, able to treat low grade concentrates, SX-EW for copper, conventional materials of construction

• Pyrite is the catalyst for chalcopyrite and enargite concentrate leaching

• Activated carbon is added to catalyze leaching of enargite \((\text{Cu}_3\text{AsS}_4)\)
GALVANICALLY ASSISTED CHALCOPYRITE LEACHING

Anodic Site

Cathodic Site

Cu$^{2+}$

Fe$^{2+}$

Cu$^{2+}$

Fe$^{3+}$

Fe$^{2+}$

Py

Cp

S$^0$

Py

GALVANICALLY ASSISTED CHALCOPYRITE LEACHING
CHALCOPYRITE CONCENTRATE #1 – 35% Cu
Effect of pyrite addition (50 g con, 65 g acid, 470 mV, 80 C)
Galvanox™ for Enargite – with Pyrite

Copper extraction
With pyrite/enargite Mixtures under Galvanox™ conditions

% Cu Dissolution vs. Time (hours) for different ratios of Py : En.
Galvanox™ for Enargite – with Activated Carbon

![Graph showing Cu Extraction over Time with two different conditions: 90 g concentrate + 100 g activated carbon and 90 g concentrate alone. The graph indicates a higher and faster Cu Extraction rate with the combined condition compared to the single concentrate.](image-url)
Total Pressure Oxidation

- Total Pressure Oxidation is an OLD technology
- 1950’s (Berezowsky, Notes for Hydro 2003 Course)
  - Garfield Cobalt Refinery (Calera Mining Co.)
  - Fredericktown Metals Refinery (National Lead)
- Widely used for gold, copper (Bagdad/Kansanshi/Sepon)
- Total Pressure Oxidation Chemistry
  - \( \text{Cu}_3\text{AsS}_4 + 8.75\text{O}_2 + 2.5\text{H}_2\text{O} \rightarrow 3\text{CuSO}_4 + \text{H}_2\text{SO}_4 + \text{H}_3\text{AsO}_4 \)
- What happens to arsenic?
- Need a source of iron to form Fe-As precipitate
GARFIELD COBALT REFINERY
(Calera Mining Company)

- Blending of feed for Fe:As control, to precipitate ferric arsenate
- Total oxidation at 190 to 240° C, 3500 kPa (air)
- 95 to 97% cobalt extraction
- Main product cobalt: 1100 t/a

<table>
<thead>
<tr>
<th>% Co</th>
<th>% Ni</th>
<th>% As</th>
<th>% Fe</th>
<th>% S</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.5</td>
<td>1.0</td>
<td>24</td>
<td>20</td>
<td>29</td>
</tr>
</tbody>
</table>

Berezowsky
Freeport Bagdad Single Autoclave
(3.5 m dia X 16.1 m length)
Leaching Summary

- Arsenic levels in ores and concentrates are increasing (generally) and may be managed by hydrometallurgical extraction and precipitation
- The best place to do this is at mine site to minimize the dispersion of arsenic
- Emerging alternatives for chalcopyrite copper concentrate treatment may be considered for treatment of high arsenic concentrates

Arsenic Precipitation with Iron

- Important to produce the right conditions in or out of the copper leach that fixes arsenic as a ferric co-precipitate
Iron Co-Precipitation with Ferrihydrite (Krause and Ettel, 1989)

Solubility of Scorodite, FeAsO$_4$.2H$_2$O at 23 °C

Effect of Fe/As Ratio at pH=5
High Temperature Pressure Oxidation (Monhemius and Swart)

Fe added as Fe(III)/Fe(II) solution or Hematite, iron sludge, ferrihydrite, pyrite

As added as As(III)/As(V) solution Or As$_2$S$_3$ or As$_2$O$_3$

Final liquor containing majority of Base metals with acid recycled

Crystalline scorodite with <2-3% base metals

Autoclave ~200 °C with 1-2 h
Residence time, ~2500 kPa with O$_2$
Maximum free acid 60-70 g/L H$_2$SO$_4$
Atmospheric Scorodite

- Demopoulos and Ecometales - control supersaturation through careful pH control
- Dowa Mining – control supersaturation by slow oxidation of ferrous sulfate/arsenic containing solutions
The Ecometales Scorodite Circuit

Ferric Sulfate

H₂O₂ (50%)

CaCO₃ (18%)

PLS from dust leach With As(III) And As(V)

As Oxid’n

Scorodite/Gypsum Precipitation

PLS <300 mg/L As Filtrate and Washate

Seed Recycle

H₂O

Product

Filtration

Scorodite/Gypsum To Impoundment

Filtrate and Washate

pH in Precipitation, October

Operational Day
Atmospheric Precipitation of Scorodite

- Well grown solids (20-30 µm)
- Excellent S/L separation & washing characteristics
Simplified Dowa Process (Fujita et al)

High Arsenic Bearing Materials (Arsenic sulfide, liberator slimes)

Oxygen

Leaching

Residue to Cu Smelter

Oxidizing Agent

Oxidation

Oxidized Soln

FeSO$_4$.7H$_2$O + O$_2$ Gas

Crystallization

Scorodite to Disposal

Solution to further treatment
SEM Pictures of Precipitated Samples (Dowa)
Outotec Process (Hydrothermal Stabilization)

- **Oxidation**
- **Fe/As Prec.**
- **Purification**
- **Hydrothermal Conversion**

- As Soln
- Oxidant
- Fe Soln

- Neut Agent
- Fe Soln

- Purification Precipitation

- Ferric Arsenate
- Ferric Arsenate

- Effluent

- Ferric Arsenate
- Scorodite
Summary

• Arsenic should be left at the minesite in a stable form
• There are a range of hydrometallurgical technologies that can extract copper from copper-arsenic concentrates (enargite)
• These technologies may be combined with the knowledge and practice related to arsenic precipitation and stabilization (Fe-As materials)
• At UBC work is underway to develop flowsheets for this purpose