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-H$_2$O Eh-pH Diagram at 25 $^\circ$ C with 0.1 mol/kg H$_2$O 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>$P_{0.0%}$</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>$P_{25.7%}$</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>$P_{50.0%}$</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>
</tr>
<tr>
<td>$P_{70.0%}$</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>$P_{90.0%}$</td>
<td>30.0</td>
<td>0.042</td>
<td>0.272</td>
<td><strong>3.65</strong></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>$P_{95.0%}$</td>
<td>34.0</td>
<td>0.102</td>
<td>0.410</td>
<td><strong>5.63</strong></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>$P_{100.0%}$</td>
<td>51.1</td>
<td><strong>7.25</strong></td>
<td>7.50</td>
<td><strong>9.28</strong></td>
<td><strong>12.7</strong></td>
<td>1.03</td>
<td>1.91</td>
<td>0.072</td>
<td>0.250</td>
</tr>
</tbody>
</table>

Simplified Flowsheet

Copper Ore or Concentrate

Reagents

Copper Leaching

As?

Wash Water

S/L Separation

Precious Metal Recovery

Gold and Silver

Final Residue

Raffinate

Copper SX-EW

Copper Cathode

Bleed

As?
# 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</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>
<td></td>
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<tr>
<td>Albion Process</td>
<td>P</td>
<td>85</td>
<td>1</td>
<td>Yes</td>
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<td>No</td>
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<tr>
<td>AAC-UBC</td>
<td>P/C</td>
<td>150</td>
<td>12</td>
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<td>No</td>
<td>Yes</td>
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<tr>
<td>Bactech/Mintek Low T Bioleach</td>
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<td>No</td>
<td>No</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>
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<tr>
<td>CESL Process</td>
<td>C</td>
<td>150</td>
<td>12</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Chalcocite</td>
</tr>
<tr>
<td>Cobre Las Cruces</td>
<td>C</td>
<td>90</td>
<td>1</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Coal + Recycle</td>
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<tr>
<td>Dynatec</td>
<td>P</td>
<td>150</td>
<td>12</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Pre-activation/Intrastage grind</td>
</tr>
<tr>
<td>FLSMIDTH</td>
<td>B</td>
<td>85</td>
<td>1</td>
<td>No/Yes</td>
<td>No</td>
<td>No</td>
<td>Galvanic</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>Chalcocite</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>
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</tr>
<tr>
<td>PLATSOL</td>
<td>P</td>
<td>225</td>
<td>32</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Chalcocite</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></td>
</tr>
<tr>
<td></td>
<td></td>
<td>220 – FeS₂</td>
<td>32</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Chalcocite</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+}

Cp

SO

4 e^{-}

4 Fe^{3+}

4 Fe^{2+}
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
Galvanox™ for Enargite – with Activated Carbon

![Graph showing copper extraction over time for different conditions.](image)
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)

<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>

- 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

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
Ferric Sulfate

H$_2$O$_2$ (50%)

CaCO$_3$ (18%)

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

As Oxid'n

Scorodite/Gypsum Precipitation

Filtrate and Washate

PLS <300 mg/L As

Seed Recycle

H$_2$O

Product

Scorodite/Gypsum To Impoundment

Filtration

pH in Precipitation, October
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$$\cdot$7H$_2$O + O$_2$ Gas

Crystallization

Solution to further treatment

Scorodite to Disposal
SEM Pictures of Precipitated Samples (Dowa)
Outotec Process (Hydrothermal Stabilization)

- Oxidation Fe/As Prec.
- Purification Precipitation
- Neut Agent Fe Soln
- Effluent
- Ferric Arsenate
- Ferric Arsenate
- Hydrothermal Conversion
- L/S
- As Soln Oxidant
- Fe Soln
- Oxidant 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