Design of Copper Hydrometallurgy Plants for High Grade Ores and Copper Concentrates

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Outline

• Leaching of High Grade Ores and Concentrates

• Design Factors
  – Copper Extraction
  – S/L Separation and Washing
  – Acid Balance
  – Copper SX-EW
  – Precious Metal Recovery

• Other Factors

• GALVANOX – New Technology for Copper Leaching

• Concluding Remarks
Leaching of High Grade Ores and Concentrates

- Developments are primarily related to leaching of high grade chalcocite – pyrite ores and leaching of chalcopyrite concentrates.
- Leaching of chalcopyrite is complicated by “passivation” of chalcopyrite under mild conditions.
- Most chalcopyrite leaching technologies try to overcome this passivation by one or more techniques.
- This is the critical feature of the overall process – without high copper extraction, the process will not be feasible.
Cu-Fe-S-H$_2$O Diagram
Strategies for Avoiding Passivation

- Leach at potential/pH that avoids passivation (Galvanic Processing).
- Add silver to avoid copper polysulfide (too expensive).
- Fine grind to P80 of less than 10 μm (mineral leaches before passivation).
- Use high temperature (+200 C) or aggressive conditions (transpassive).
- Use chloride or chloride addition.
- Use bacteria (thermophiles) that avoid passivation.
- Add oxidation catalyst like nitrate or nitrite (NSC).
Sulfur Chemistry

• Sulfur is formed from sulfide minerals during leaching

• Three temperature regimes

• Low T:  < 119.3 C – SOLID (S$_8$)

• Medium T:  119.3 C to 159 C – LIQUID (S$_8$)

• High T:  +159 C – LIQUID/POLYMER (S$_n$) – S Oxidized
**Low Temperature Leaching (< 119 C)**
- Elemental sulfur forms porous product layer
- Kinetics can be slow due to diffusion through sulfur product

**Medium Temperature Leaching (119-159 C)**
- Molten sulfur is dispersed by addition of a sulfur dispersant/surface active agent
- Lignin sulfonate and Quebracho are two common agents.
- Sulfide mineral becomes sulfophobic and hydrophilic and sulfur liquid droplets are dispersed

**High Temperature Leaching (+200 C)**
- Transpassive leaching – sulfur fully oxidized to sulfate
Iron Precipitation

• Dissolved iron will be oxidized and precipitated as ferric hydroxide (undesirable), jarosite, goethite or hematite

• Goethite forms at less than ° 140 C with hematite forming above 140 ° C

• Jarosite can form over wide temperature range

• Basic ferric sulfate processes (Sepon) precipitate iron at high free acid and high T (220 ° C). Iron forms basic ferric sulfates which then re-dissolve at atmospheric T+P.
## Sulfate Processes

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<th>Status</th>
<th>Temp. (^\circ\text{C})</th>
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Recent Developments

- Mt. Gordon, Australia – 50,000 tpa Cu  X (closed in 2003)
- PD/Freeport Bagdad USA – 16,000 tpa Cu  √ (now MoS$_2$)
- Alliance Copper, Chile – 20,000 tpa Cu  X (2 year demo plant)
- Sepon Copper, Laos – 90,000 tpa Cu  √
- Kansanshi, Zambia – +50,000 tpa Cu  √
- PD/Freeport Morenci USA – 75,000 tpa Cu  X (long story)
- Cobre Las Cruces, Spain – 72,000 tpa Cu  √
- CESL Process, Vale Brazil – 10,000 tpa Cu  X (short term demo plant)
Mount Gordon Autoclaves
(2X120m³ Capacity)
Cobre Las Cruces
8 X 350 m³ OKTOP Reactors
BIOCOP Bioleach Tanks (Chile) 
~ 4 days of residence time
Freeport Bagdad Single Autoclave
(3.5 m dia X 16.1 m length)
Solid-Liquid Separation

• The washing of leach residues may be done with;
  – Countercurrent decantation (6-7 stages)
  – Vacuum belt filter (with 2-3 stages of washing)
  – Pressure filter (with washing)

• Wash solutions may include;
  – Water
  – Raffinate (to close water balance)

• Washing may be intended to recovery
  – Copper
  – Iron/Acid

• Process selection based on testwork and economic tradeoff
Sepon Copper
( Clarifier, 4 Raff CCD’s, 3 Water CCD’s )

Khanong Copper Orebody
Gold Operation

Padan Camp

Copper Operation
Mount Gordon Residue Filter – 158 m² for ~750,000 tpa ore treatment rate
Acid Balance (and Oxygen Consumption)

• Acid generation must be balanced with acid consumption

• Partial versus total oxidation
  – \( \text{CuFeS}_2 + 4.25\text{O}_2 + \text{H}_2\text{O} = \text{CuSO}_4 + 0.5\text{Fe}_2\text{O}_3 + \text{H}_2\text{SO}_4 \)
  – \( \text{CuFeS}_2 + \text{O}_2 + 2\text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{FeSO}_4 + 2\text{H}_2\text{O} \)

• Full Oxidation
  – 2.15 t of oxygen/t Cu
  – 3.09 t of acid/t Cu (same as smelting)

• Partial Oxidation
  – 0.5 t of oxygen/t Cu
  – NO Net Acid Production

• Acid may be used for associated heap/dump leach

• If no or little acid consumption, minimize sulfur oxidation
Acid Balance (and Oxygen Consumption)

• Acid can also be generated by pyrite

\[
\text{FeS}_2 + 3.75\text{O}_2 + 2\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 2\text{H}_2\text{SO}_4
\]

• Mount Gordon and Cobre Las Cruces – Modest Pyrite Oxidation to make up acid (and iron)

• Mount Gordon – target was 2-3 % Pyrite Oxidation

• Cobre Las Cruces – target is 3-5% Pyrite Oxidation

• Sepon – pyrite and sulfur are floated from the atmospheric leach tailing to make high “S” feed to the high temperature autoclave
Freeport Bagdad Flowsheet (140 t/d H₂SO₄ to Heap (Stockpile) Leach (Marsden, 2003)
A BRIEF LOOK AT KANSANSHI MINE PROCESS

MINING
Ore mined = 24,506,000t

SULPHIDE
Ore mined = 8,855,000t
Grade = 0.7%Cu
Rec. = 91%

CRUSHING & MILLING

MIXED
Ore mined = 8,377,000t
Grade = 1%Cu
Rec. = 63%

CRUSHING & MILLING

OXIDE
Ore mined = 6,072,000t
Grade = 2.3%Cu
Rec. = 85%

CRUSHING & MILLING

SULPHIDE FLOTATION

MIXED FLOTATION

OXIDE FLOTATION

Concentrate
22.3%Cu

HYDROMET
Leaching
Solvent Extraction
Electrowinning

HPL

PLS

Oxide Leach Tails

Grade A Cathode

TO SMelters

TSF (Oxide)

TSF (Sulphide)

Tails

Oxide Float Tails
Sepon Flowsheet

9 t/h of Pyrite/Sulfur to total pressure oxidation
Copper SX-EW

- Transfer of copper from strong leach solutions to Cu EW
- Solvent extraction with oximes preferred
- Freeport pioneered direct EW
- Sepon – control of copper concentration in PLS to produce low Cu in raffinate for wash
Precious Metal Recovery

• Au may be recovered by cyanidation of copper leach residues.

• However if S present then form SCN and increase the cost of Au recovery.

• Ag often forms Ag-jarosite under copper leaching conditions. May have to use lime boil to decompose Ag-jarosite prior to cyanidation.

• Alternative strategy to use other reagents (e.g. S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}, SCN\textsuperscript{-} or Cl\textsuperscript{-}/Br\textsuperscript{-})

• PGM Recoveries difficult from residues but possible directly (PLATSO\textsuperscript{TM})
Other Factors in Design

• Arsenic and minor elements – co-precipitation with iron

• Gypsum scaling – when cooling, try to do so in the presence of solids as “seed”

• Sepon – Cooling tower treats pulp

• Cobre Las Cruces – Cooling tower sees thickener O/F solution

• Materials of construction – high temperatures and pressures (if used) are deleterious for many materials in the presence of acid-copper-iron sulfate solution

• Especially difficult in autoclaves (lots of experience from gold and base metal autoclaves)
Sepon Flowsheet

9 t/h of Pyrite/Sulfur to total pressure oxidation
LEACH CIRCUIT

Cobre Las Cruces
La nueva industria minera de Andalucía

Capacity  t/d  3,562
Availability  %  90
Raffinate  m³/h  313
(FeT)Req  g/L  50
Fe³⁺/Fe²⁺  1
Temperature  °C  90
Leach time  h  8
Copper extraction  %  91.8
(Cu²⁺)PLS  g/L  43
Oxygen Consumption  t/h  6.6
Acid Consumption  kg/t  20
GALVANOX™ PROCESS

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

• Atmospheric leaching of chalcopyrite
GALVANOX FEATURES

- Atmospheric Leach (≈ 80° C)
- No microbes
- Pure sulphate medium (no chloride)
- No fine grinding
- Generates elemental sulfur (> 95%), low oxygen demand
- No surfactants
- Selective for chalcopyrite over pyrite (can cost-effectively treat low grade concentrates down to 9% copper or less)
- Complete copper recovery, typically in less than 12 hours, and sometimes in as little as 4 hours
- Fully compatible with conventional SX-EW
- Conventional materials of construction
GALVANOXCHEMISTRY

- GALVANOX takes advantage of the galvanic effect between chalcopyrite and pyrite.

- Chalcopyrite is a semiconductor, and therefore corrodes electrochemically in oxidizing solutions.

- In ferric sulphate media, the overall leaching reaction is as follows:

  \[
  \text{CuFeS}_2 + 2 \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{CuSO}_4 + 5 \text{FeSO}_4 + 2 \text{S}^0
  \]

- This reaction may be represented as a combination of anodic and cathodic half-cell reactions:

  **Anodic:** \( \text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2 \text{S}^0 + 4 \text{e}^- \)

  **Cathodic:** \( 4 \text{Fe}^{3+} + 4 \text{e}^- \rightarrow 4 \text{Fe}^{2+} \)
UNASSISTED CHALCOPYRITE LEACHING

Cu^{2+} \ Fe^{2+} \ 4 \ Fe^{3+} \ 4 \ Fe^{2+} \ S^{0} \ e^{-} \ CuFeS_{2} 

Anodic Site

Cathodic Site
GALVANOX RATE CONTROL

- Chalcopyrite appears passivated
- Anode passivation due to iron depleted sulphide
- Anode or cathode?
- Dixon and Tshilombo – passivation appears to be at cathode (ferric reduction)
- Pyrite catalyzes the cathodic process in galvanic leaching
- Pyrite is inert and can be recycled
GALVANICALLY ASSISTED CHALCOPYRITE LEACHING

Anodic Site

Cu^{2+}

Fe^{2+}

Cp

Py

4 e^-

Cathodic Site

4 Fe^{3+}

4 Fe^{2+}

S^0

GALVANICALLY ASSISTED CHALCOPYRITE LEACHING
GALVANICALLY ASSISTED CHALCOPYRITE LEACHING

Partially leached particle

Completely leached particles
GALVANOX CHEMISTRY

- The ferric required for GALVANOX leaching is regenerated *in situ* with oxygen gas

Ferric leaching of chalcopyrite:

\[
\text{CuFeS}_2 + 2 \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{CuSO}_4 + 5 \text{FeSO}_4 + 2 \text{S}^0
\]

Oxidation of ferrous with dissolved oxygen gas:

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

Overall leaching reaction:

\[
\text{CuFeS}_2 + \text{O}_2 + 2 \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{FeSO}_4 + 2 \text{S}^0 + 2 \text{H}_2\text{O}
\]

Conventional SX-EW of Cu and Fe Precipitation
In summary, the overall GALVANOX process chemistry is as follows:

Galvanically-assisted atmospheric leaching of chalcopyrite:

\[ \text{CuFeS}_2 + \text{O}_2 + 2 \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{FeSO}_4 + 2 \text{S}_0 + 2 \text{H}_2\text{O} \]

Iron oxyhydrolysis:

\[ \text{FeSO}_4 + \frac{1}{4} \text{O}_2 + \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{Fe}_2\text{O}_3 (s) + \text{H}_2\text{SO}_4 \]

Copper electrowinning:

\[ \text{CuSO}_4 + \text{H}_2\text{O} \rightarrow \text{Cu}^0 + \frac{1}{2} \text{O}_2 \uparrow + \text{H}_2\text{SO}_4 \]

Overall process chemistry:

\[ \text{CuFeS}_2 + \frac{5}{4} \text{O}_2 \rightarrow \text{Cu}^0 + 2 \text{S}_0 + \frac{1}{2} \text{O}_2 \uparrow + \frac{1}{2} \text{Fe}_2\text{O}_3 (s) \]
BATCH TESTING

- Six 3-L jacketed reactors
- Water baths for temperature control
- Digital oxygen mass flow meters for potential control
- Automated data acquisition for potential, pH and temperature
CHALCOPYRITE CONCENTRATE #1 – 35% Cu
Effect of pyrite addition (50 g con, 65 g acid, 470 mV, 80 C)
CHALCOPYRITE CONCENTRATE #2 – 23.6 % Cu
Effect of pyrite addn (30 g con, 120 g Py, 30 g acid, 480 mV, 80 C)
CHALCOPYRITE CONCENTRATE #3 – 24.1 % Cu
Effect of pyrite addn (10 g con, 40 g Py, 15 g acid, 470 mV, 80 C)
CHALCOPYRITE CONCENTRATE #4 – 20.1 % Cu
Effect of pyrite addn (57 g con, 112 g Py, 60 g acid, 450 mV, 80 C)
CHALCOPYRITE BULK CONCENTRATE – 10.2% Cu
(150 g bulk con @ ~1.21 Py/Cp ratio, 75 g acid, 440 mV, 80 C)
Conclusions

• Hydromet has advanced by;

• **Necessity**
  – Mount Gordon
  – Sepon
  – Cobre Las Cruces

• **Opportunity**
  – Bagdad
  – Kansanshi

• **New Process Developments**
  – Galvanox

• Future is bright for hydromet 😊
Thank You!

Any Questions?