New Developments in the Atmospheric and Pressure Leaching of Copper Ores and Concentrates

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Copper Solvent Extraction – Hydroxyoxime

The Enabling Technology
Copper Leach–Solvent Extraction–Electrowinning

- Limited to oxidized ores of copper or leachable sulfides
- Approximate 20% of world copper supply is recovered by this method
- 80% is still recovered by smelting and refining of chalcopyrite ($\text{CuFeS}_2$) concentrates
- May be desirable to extend hydrometallurgical treatment to chalcopyrite ores and concentrates
- May also be desirable to treat high arsenic concentration ores directly (limit of 0.5% As)
- Where does the technology stand?
- Focus on Sulfate Based Processes
Copper Ore/Concentrate Treatment

• Focus on Sulfate Processes
• Variety of Process Options Available
• Key Factors
  – Copper Extraction
  – Iron Precipitation
  – Precious Metal Recovery
  – Sulfur Deportment
  – Cost!
Process Options

• Copper Leaching Issues;
  – Chalcocite leaches easily in ferric sulfate solution
  – Copper leaching controlled by copper mineral leach kinetics
  – Chalcopyrite passivates under mild conditions
  – Liquid sulfur wets unreacted minerals and stops leaching
Chalcopyrite Passivation

- Eh – pH Diagram Shows Many Phases between CuFeS$_2$ (solid) and CuSO$_4$(aqueous)

- Chalcopyrite is Believed to Passivate by Formation of an Iron-Deficient Copper Sulfide (CuS$_n$)
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.
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 (eg. \(S_2O_3^{2-}\), SCN\(^-\) or Cl\(^-\)/Br\(^-\))
- PGM Recoveries difficult from residues but possible directly (PLATSOL\(^{TM}\))
### Historical Processes

<table>
<thead>
<tr>
<th>Anaconda Arbiter Process</th>
<th>UBC Cominco</th>
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<tr>
<td>Sherritt Gordon</td>
<td>Etc!</td>
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<td>Sherritt Cominco</td>
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Hazen Research 1999 – 43 Copper Processes Tested – None achieved sustained commercial practice

None of these are working anywhere today!
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<th>Process</th>
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<th>Temp. (°C)</th>
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Recent Developments

- Mt. Gordon, Australia – 50,000 tpa Cu \( \times \) (closed in 2003)
- PD/Freeport Bagdad USA – 16,000 tpa Cu \( \checkmark \) (now MoS\(_2\))
- Alliance Copper, Chile – 20,000 tpa Cu \( \times \) (2 year demo plant)
- Sepon Copper, Laos – 90,000 tpa Cu \( \checkmark \)
- Kansanshi, Zambia - +50,000 tpa Cu \( \checkmark \)
- PD/Freeport Morenci USA – 75,000 tpa Cu \( \times \) (long story)
- Cobre Las Cruces, Spain – 72,000 tpa Cu \( \checkmark \)
- CESL Process, Vale Brazil - 10,000 tpa Cu \( \times \) (short term demo plant)
The SEPON Copper Project

- Project located in a remote area of eastern Laos, South East Asia, little infrastructure support locally.

- The copper mineralogy is predominantly chalcocite contained within weathered sediments (clay). Some pyrite in ore.

- At feasibility, resource contained 700,000t of copper metal at an average grade of 5.1% copper.

- Plant designed to produce 60,000t/a LME Grade A copper cathode at an overall copper recovery of 90%. Now +90,000t/a

- The plant started in March 2005.

- Cash costs were estimated at 40c/lb copper

- Full capital cost was $227 M USD (for initial 60,000 tpa Cu plant)

- Ramp up to nameplate production within 9 months
SEPON LOCALITY MAP
Sepon Process Chemistry

- Process Chemistry Summary:
  - Acid leach of carbonate copper (Malachite, Azurite)
  - Ferric Leach of sulfide copper (Chalcocite)
  - Ferric provided by pressure oxidation of Pyrite concentrate
  - Ore is milled in raffinate to close water balance and provide preleaching of copper
  - Remaining copper leaching done atmospherically at 80 C, 5hr
  - Ferric regeneration via air addition during Atm. Leach

Copper Leaching Reaction via Ferric

\[ \text{Cu}_2\text{S} + 2\text{Fe}_2(\text{SO}_4)_3 \rightarrow 2\text{CuSO}_4 + \text{S} + 4\text{FeSO}_4 \]

(Chalcocite)
Sepon Autoclave Process Chemistry

- Process Chemistry

- Pyrite Oxidation to form ferric sulfate
- Precipitation of ferric sulfate
- 2 possible products at 220°C
  - Hematite or Basic Ferric Sulfate (BFS)

- What Controls product formation – Free Acid Level
  - Greater than 65-70g/L free acid makes BFS

Pyrite Oxidation to Ferric Sulfate

$$2\text{FeS}_2 + \frac{15}{2}\text{O}_2 + \text{H}_2\text{O} = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$$

Equilibrium between Hematite and BFS

$$\text{Fe}_2\text{O}_3 + 2\text{H}_2\text{SO}_4 = 2\text{FeOHSO}_4 + \text{H}_2\text{O}$$
Sepon Autoclave Process Chemistry

Process Chemistry Summary:

- BFS Re-dissolves during pressure let down in Flash Vessel
- Further dissolution occurs in designated BFS re-leach tanks; acid added via CCD wash solution with temperature maintained around 95-97°C
- Hot ferric rich solution added to fresh leach ore feed prior to atmospheric leaching

BFS Dissolution to Ferric Sulfate

\[ 2\text{FeOHSO}_4 + \text{H}_2\text{SO}_4 = \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \]
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<td>Galena</td>
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SEPON Copper Plant

Khanong Attributes
- High grade
- Near surface
- Leachable
- Hydro power
- Long life
- Upside

Khanong open pit
Gold Plant
Crush & Grind
Copper ROM Pad
Leach area
Oxygen plant
CCD Train
Solvent Extraction
Electro-winning
WHOLE ORE LEACH

- Whole ore leach was effective at leaching copper from copper sulfides using a ferric/ferrous chemical couple in an acid solution

- **Challenge of nature**: the ore consumes acid and the cost of acid is prohibitive in Laos

- **Solution**: Make ferric sulfate/sulfuric acid solutions by recovering sulfur and pyrites from leach residue (by flotation) and oxidizing under water in a pressure leach autoclave
Cobre Las Cruces
La nueva industria minera de Andalucía

LOCALIZACIÓN DEL PROYECTO

FRANJA PIRÍTICA IDÉRICA
- Cobertura terciaria
- Cobertura paleozoica (Guím)
- Sulfuros masivos (>), rocas volcánicas, sedimentarias e intrusiones

OTRAS FORMACIONES GEOLÓGICAS
- Paleozoico a mesozoico

Principales yacimientos metálicos

PORTUGAL  ESPAÑA

Océano Atlántico
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<td>KTons</td>
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HYDROMETALLURGICAL PLANT
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<tr>
<td>Ore Grade</td>
<td>% Cu</td>
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<td>Copper Production</td>
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<tr>
<td>Total Copper</td>
<td>t</td>
<td>1,000,000</td>
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<tr>
<td>Project Life</td>
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LEACH CIRCUIT

Cobre Las Cruces
La nueva industria minera de Andalucía

Capacity t/d 3,562
Availability % 90
Raffinate m³/h 313
(FeT)Ref g/L 50
Fe³⁺/Fe²⁺ 1
Temperature ºC 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
Cobre Las Cruces Commissioning and Rampup

- Slower rampup due to a number of issues
- Grinding thickener UF density < 80% Solids – Fe washout
- Filtration difficulties – Fe washout
- Maintenance (chloride + acid + 90 C)
- Gas-liquid mass transfer in OKTOP’s improved by;
  - Increase in leach surge capacity ahead of OKTOP’s to destroy carbonates
  - Improvement in sparger system
- Plant is now close to or at design of 72,000 tpa of Cu
Total Pressure Oxidation

- Copper sulfide minerals are rapidly decomposed by high temperature oxidation conditions.
- Rapid and complete copper leaching, high degree of iron hydrolysis and impurity fixation.
- Complete sulfur oxidation with high oxygen consumption.
- Copper recover from the oxidation solution can be accomplished by SX-EW.
- **Acid is available as a by-product.**
- Au and Ag can be recovered by cyanidation of washed residue.
Autoclaving of Copper Concentrates

$$2\text{CuFeS}_2(s) + \frac{17}{2}\text{O}_2(g) + 2\text{H}_2\text{O} \rightarrow 2\text{CuSO}_4(aq) + \text{Fe}_2\text{O}_3(s) + 2\text{H}_2\text{SO}_4(a)$$
Reference from Hydro 2003

- **COPPER CONCENTRATE LEACHING DEVELOPMENTS BY PHELPS DODGE CORPORATION**
- John O. Marsden, Robert E. Brewer and Nick Hazen
- Information in next slides is from this presentation
- Also followup presentation to Copper 2007 Short Course
Freeport Total Pressure Oxidation at Bagdad Arizona

• Total Pressure Oxidation at 220 – 230 C

• US $40 Million for 16,000 tpa Cu Leach SX/EW plant (brownfields)

• Copper is leached and then merged into existing heap leach copper recovery system

• Acid from TPOX is used beneficially in heap leach portion of Bagdad plant

• Economic credit for acid is applied to TPOX plant
Copper Extraction and Sulfide Oxidation from Pilot Plant Compartment Samples

![Graph showing copper extraction and sulfide oxidation over cumulative residence time.](image-url)
## Process Design Criteria

<table>
<thead>
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<th>Parameter</th>
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<td>Overall copper recovery</td>
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<td>H₂SO₄</td>
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Marsden et al
Marsden et al.
Plant Description

- The concentrate leaching plant consists of:
  - concentrate repulping system
  - pressure leaching
  - flash let-down and gas scrubbing
  - four stages of countercurrent decantation
  - a four-stage solid residue neutralization system
  - a copper-bearing solution storage pond

- Modifications to SX and expansion of EW

- Ancillary facilities include an oxygen plant

- Sulfuric Acid Production - 140 tons of sulfuric acid per day into the copper-bearing leach solution.

- The concentration is ~ 40 g/L H2SO4.

- Provides acid self sufficiency for Bagdad stockpile heap leach

- Economic credit for acid is applied to concentrate leaching process – this is essential for economic viability
PLV Building View
Feed and Products

Concentrate    Strong PLS    Residue
A BRIEF LOOK AT KANSANSHI MINE PROCESS

MINING
Ore mined = 24,506,000 t

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

CRUSHING & MILLING

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

CRUSHING & MILLING

SULPHIDE FLOTATION

TO SMELTERS

TSF (Oxide)

TSF (Sulphide)

MIXED
Ore mined = 8,377,000 t
Grade = 1.1% Cu
Rec. = 63%

MIXED FLOTATION

CRUSHING & MILLING

OXIDE FLOTATION

Concentrate
22.3% Cu

HYDROMET
Leaching
Solvent Extraction
Electrowinning

HPL

PLS

Oxide Leach Tails

Oxide Float Tails

Grade A Cathode
Enargite Leaching using the Galvanox Process

- Process developed by David Dixon and his student at UBC
- Initial Galvanox process uses pyrite/chalcopyrite mixtures to catalyze the leaching of chalcopyrite
- The study of enargite ($\text{Cu}_3\text{AsS}_4$) leaching has shown that the process can be extended to high arsenic concentrates
- In this case the catalyst is activated carbon (same as used for gold leaching)
- Using activated carbon, the enargite can be oxidized and importantly, the arsenic can be leached and precipitated.
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
GALVANOX CHEMISTRY

- 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

Unassisted chalcopyrite leaching is a process where copper and iron sulfide minerals react with an oxidizing agent, typically sulfuric acid, to release copper and iron in an ionic form. The chemical equation for this process is:

\[ \text{Cu}^{2+} + \text{Fe}^{2+} + 4 \text{Fe}^{3+} + 4 \text{e}^- \rightarrow 4 \text{Fe}^{2+} + \text{CuFeS}_2 + \text{SO}_4^{2-} \]

The figure illustrates the reaction at two sites: anodic and cathodic sites. At the anodic site, copper ions and iron ions are oxidized to copper ferric sulfide and sulfuric acid, releasing electrons. At the cathodic site, iron ions are reduced back to iron ions, consuming the released electrons.

The diagram shows the flow of ions and electrons as follows:

- **Cu^{2+}** flows from the left side to the anodic site, where it participates in the oxidation reaction.
- **Fe^{2+}** flows from the left side to the anodic site, where it is oxidized.
- **SO_4^{2-}** flows from the cathodic site to the right side, where it is produced.
- **4 e^-** flows from the anodic site to the cathodic site, balancing the electron transfer.
- **CuFeS_2** is produced at the anodic site.
- **4 Fe^{3+}** flows from the anodic site to the right side, where it is consumed.
- **4 Fe^{2+}** flows from the cathodic site to the right side, where it is produced.

The figure on the right side of the diagram represents a typical mineral particle, where the leaching process occurs on the surface of the mineral.
UNASSISTED CHALCOPYRITE LEACHING
GALVANOX RATE CONTROL

- Chalcopryrite 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
GALVANICALLY ASSISTED CHALCOPYRITE LEACHING

Partially leached particle

Completely leached particles
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 BULK CONCENTRATE – 10.2% Cu
(150 g bulk con @ ~1.21 Py/Cp ratio, 75 g acid, 440 mV, 80 C)
Enargite Leaching
Effect of catalyst addition

Cu extraction (%)

Time (hours)

1:1 carbon
No carbon

23% En, 4% Cp, 62% Py
Effect of catalyst addition

- 1:1 carbon added after 69 hours

**Cu extraction (%)**

**Time (hours)**

- Carbon added

62% En, 7% Tn, 16% P
Effect of catalyst addition
Effect of activated carbon

SEM cross-section micrographs of enargite particles leached for 19 h

a) without a carbon catalyst, b) with a carbon catalyst.
Effect of carbon recycle

46% En, 7% Cp, 5% Tn, 35% Py
Effect of carbon recycle

![Graph showing the effect of carbon recycle on initial rate of copper extraction and final copper extraction. The graph displays the number of times the catalyst was used on the x-axis, with columns indicating the initial rate of copper extraction and lines connecting the final copper extraction values.]
Effect of solution potential

Cu extraction (%)

Time (hours)

530 mV
515 mV
490 mV
450 mV

23% En, 4% Cp, 62% Py
Effect of stirring speed

Time (hours)

Cu extraction (%)

- 1200 rpm
- 1000 rpm
- 800 rpm

46% En, 7% Cp, 5% Tn, 35% Py
Pilot Plant Operation

• Two pilot plants have been performed on the enargite version of the process

• The first pilot plant was just for leaching and showed that enargite could be leached to high extraction in a continuous mode

• The second pilot plant was an integrated pilot plant (right to Cu SX-EW) and showed that the process could be integrated – once again with high projected copper extractions

• David Dixon and his industrial partners are continuing to advance the understanding and the application of the technology.
Conclusions

- Copper Hydromet has advanced by;

- **Necessity**
  - Mount Gordon
  - Sepon
  - Cobre Las Cruces

- **Opportunity**
  - Bagdad
  - Kansanshi

- Many possible processes available for treatment of chalcopyrite concentrates (opportunity)

- The Galvanox process is promising for treatment of high arsenic concentrates (necessity)

- Future is bright for copper hydromet 😊
Thank You!

Any Questions?