New Developments in Cu and Ni Hydrometallurgy
Presentation to JOGMEC (Japan)
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University of British Columbia
Purpose

• To highlight selected developments in the hydrometallurgical extraction of copper and nickel from their raw materials.
General Comments
Metal Recovery Flowsheet

Metal Bearing Raw Materials

Metal Extraction

Metal Purification

Metal Recovery

Reagents

Waste Products to Disposal

Impurities

Water and Reagent Recycle

Metal Products to Market

Metal Products to Market
Metal Bearing Raw Materials

- Lower content of metals of interest
- More complex assemblages
- Increasing recycling of industrial and post consumer wastes
- Must recover all metals of value to the maximum extent for economic feasibility
Reagents

- Oxygen, Hydrogen, Chlorine, Salts, Acids, Bases, Organics.....
- Reagent Use Must be Minimized for Economic Efficiency
- Reagents Must not Result in Environmental Harm
Metal Recovery Flowsheet

Metal Bearing Raw Materials

- Reagents
  - Metal Extraction
    - Metal Purification
      - Metal Recovery
        - Waste Products to Disposal
        - Impurities
        - Metal Products to Market

- Water and Reagent Recycle
Waste Products to Disposal

• Essential to Properly Dispose of all Waste Products (Solid/Solution/Gas)
• Disposal is for the Long Term
Metal Purification

- Common and novel separation technologies applied to metal purification and concentration
- Solvent extraction, ion exchange, electrochemistry, precipitation, etc.
- Novel membrane and “molecular recognition” technologies are advancing the ability to separate and recover minor metals
Hydroxy – oxime complexation of copper from solution

~ 25% of the world’s copper is recovered via this complex!
Metal Recovery Flowsheet

Metal Bearing Raw Materials

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Impurities

Metal Recovery

Water and Reagent Recycle

Metal Products to Market
Water and Reagent Recycle

• Water is recycled to avoid having to treat any water for release
• Reagents are recycled to reduce cost and generation of excess waste
Metal Recovery Flowsheet

Metal Bearing Raw Materials

Metal Extraction

Metal Purification

Metal Recovery

Reagents

Waste Products to Disposal

Impurities

Water and Reagent Recycle

Metal Products to Market
Metal Products to Market

- Final metal products must be exceptionally pure – often 3, 4 or 5 “9”s in purity
- Small amounts of impurities can render metal un-saleable or reduce value
- Physical form is often important
- Copper is almost always metal product
- Nickel/cobalt – intermediates favoured
Copper Extraction

- Development of Non-Chalcopyrite Resources
  - Mt. Gordon, Sepon, Las Cruces – chalcocite ores
- Chalcopyrite Concentrate Leaching
  - Chemical and Bioprocessing
  - Sulfate and Chloride Media
- Heap Leaching of Copper from Chalcopyrite
  - Not covered in this talk!
  - David Dixon at UBC is working actively in this field with international sponsorship through AMIRA
  - Direct leach of CuFeS₂ ores at minesite represents the future for many operations
Nickel Extraction

• Laterite Leaching Processes
  – The future is laterites
  – HPAL, Atmospheric Leaching, Chloride Leaching and Heap Leaching

• Sulfide Leach Processes
  – The future is later! – sulfides are still very important
  – Voisey Bay Process, Activox at Tati Nickel, PLATSOL for NorthMet, Minnesota

• Integration of Laterite and Sulfide Processing
Copper Hydrometallurgy

• 20-25% of the global copper production is accomplished using hydrometallurgy
• Dominant process is copper leach – SX – EW by treatment of oxide and secondary sulfide ores
• Heap and dump leaching dominates as the leaching process
• Chalcopryite concentrates are generally smelted
• What are the prospects of replacement of smelting for chalcopryite and other concentrates?
Overview

- Copper Concentrate Treatment
  - Why?
  - What is the problem?
  - Emerging processes (Chemical and Biological)
Why Copper Concentrate Treatment?

Drivers for Innovation

- **Capital Cost.** Smelter – Refinery - US$ 3,000-5,000 per tpa of Cu.
- **Impurity Tolerance** (Se, Te, Hg, As, Sb, Bi, F, Cl).
- **Copper-Gold Concentrates.** Low grade concentrates.
- **Mine-to-Market Optimization.** Global evaluation of resource and available technology.
- **Recovery of Valuable Byproducts.** Copper concentrates often contain significant levels of base- and precious-metal byproducts.
- **Use of Existing Capital.** SX-EW plants represent significant capital investment that could be adapted to copper concentrate treatment.

Impediments to Proceeding

- **Poor Technical Results.**
- **New Technology Risk.** New processes, unique chemistry, processing conditions, or equipment – increase risk
- **Cost of Licensing.** License costs can mitigate against new technology selection.
Historical Processes

- Anaconda Arbiter Process
- Cuprex
- CLEAR
- Minemet Recherche
- Sherritt Gordon
- Sherritt Cominco
- UBC Cominco
- Dextec
- Coloso
- Noranda Antlerite Process
- Etc!

- None of these are working anywhere today!
THE PROBLEM OF LEACHING CHALCOPYRITE

• Chalcopyrite is the one of the most difficult sulfide minerals to leach.

• Passive films of copper polysulfide form with mild leaching in sulfate. May inhibit chemical or biological oxidation

• Molten sulfur wetting of chalcopyrite can also inhibit leaching

• Chalcopyrite (Cu, Fe and S)
  – Cu -> CuSO₄
  – Fe -> FeSO₄, Fe₂(SO₄)₃, Fe₂O₃, FeO(OH), H₃OFe₃(SO₄)₂(OH)₆
  – S -> S or SO₄
Oxygen Consumption in Chalcopyrite Leaching

For $S^0$ Formation
1 - 1.25 mole $O_2$/mole Cu (0.5 to 0.63 t $O_2$/t Cu).

For $SO_4^{2-}$ Formation
4.25 mol/mol Cu (2.15 t $O_2$/t Cu)
SURFACE ACTIVE AGENTS FOR SULFUR DISPERSION

Sulfur melts at 119 °C and polymerizes above 159 °C

Molten sulfur dispersion using surface active agents (surfactants)

Zinc pressure leach process - COMMERCIAL

Chalcopyrite – EMERGING – Anglo American Corporation – University of British Columbia Process
Effect of Surfactants on Sulfur. Sulfur Drops on Chalcopyrite at 150 °C

Surfactant-free
0.05 g/L lignin sulfonate
0.05 g/L Quebracho

Dreisinger and Lu – Unpublished Work
Overcoming Chalcopyrite Passivation

• Fine Grinding (5-10 um particles)
  – Passivation has an “induction time”
  – Small enough particles are leached prior to onset of passivation

• Chloride Leaching (or chloride catalyzed leach)
  – Chalcopyrite does not passivate in chloride leach

• High Temperature
  – Trans passive leaching

• Bio-catalyzed Leach
## Sulfate Processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Status</th>
<th>Temp. (°C)</th>
<th>Pressure (atm)</th>
<th>Regrind D80 (µm)</th>
<th>Special Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activox Process</td>
<td>P</td>
<td>90-110</td>
<td>10-12</td>
<td>5-10</td>
<td>Fine grinding combined with high oxygen overpressure overcomes chalcopyrite passivation</td>
</tr>
<tr>
<td>Albion Process</td>
<td>P</td>
<td>85</td>
<td>1</td>
<td>5-10</td>
<td>Atmospheric ferric leaching of very finely ground concentrate</td>
</tr>
<tr>
<td>AAC-UBC Process</td>
<td>P</td>
<td>150</td>
<td>10-12</td>
<td>10-15</td>
<td>Modest regrind combined with surfactants for chalcopyrite leaching</td>
</tr>
<tr>
<td>Bactech/Mintek Low Temperature Bioleach</td>
<td>P</td>
<td>35</td>
<td>1</td>
<td>5-10</td>
<td>Low T bioleach (35-50 C) requires very fine grind to overcome chalcopyrite passivation.</td>
</tr>
<tr>
<td>BIOCOP™ Process</td>
<td>C</td>
<td>65-80</td>
<td>1</td>
<td>37</td>
<td>High T bioleach (65-80 C) uses thermophilic bacteria</td>
</tr>
<tr>
<td>CESL Copper Process</td>
<td>D</td>
<td>140-150</td>
<td>10-12</td>
<td>37</td>
<td>Chloride catalyzed leach of chalcopyrite producing basic copper sulfate precipitate in the autoclave</td>
</tr>
<tr>
<td>Dynatec Process</td>
<td>P</td>
<td>150</td>
<td>10-12</td>
<td>37</td>
<td>Chalcopyrite is leached using low grade coal as an additive</td>
</tr>
<tr>
<td>Mt. Gordon Process</td>
<td>C</td>
<td>90</td>
<td>8</td>
<td>100</td>
<td>Pressure oxidation of chalcoite/pyrite ore or bulk concentrate in an iron sulfate rich electrolyte</td>
</tr>
<tr>
<td>PLATSOL Process</td>
<td>P</td>
<td>220-230</td>
<td>30-40</td>
<td>15</td>
<td>Total pressure oxidation in the presence of 10-20 g/L NaCl. Precious metals leached at the same time as base metals</td>
</tr>
<tr>
<td>Sepon Copper Process</td>
<td>C</td>
<td>80 – Copper 220-230 - Pyrite</td>
<td>Atm 30-40</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Total Pressure Oxidation Process</td>
<td>C</td>
<td>200-230</td>
<td>30-40</td>
<td>37</td>
<td>Extreme conditions of T and P designed to rapidly destroy chalcopyrite and other sulfides</td>
</tr>
</tbody>
</table>
Recent Developments

- Mt. Gordon, Australia – 50,000 tpa Cu
- Phelps Dodge Bagdad USA – 16,000 tpa Cu
- Alliance Copper, Chile – 20,000 tpa Cu
- Sepon Copper, Laos – 66,000 tpa Cu
- CESL Process, CVRD Brazil, 10,000 tpa Cu (under construction)
Mt Gordon
Ferric Leach Process

- Fine chalcocite coatings on pyrite
- Impossible to float high grade concentrate at suitable recovery
- Hydrometallurgy process developed
- Selective leach of copper away from pyrite
Ferric Leaching Circuit

Basic Circuit

Ground Ore or Concentrate → Leaching → Liquid/Solid Separation → Clarification → Solution 35-45g/l Fe

Oxygen

PLS

Bleed

Raffinate

Tailings

35-45g/l Fe

JOGMEC Presentation, February 2006 – New Developments in Cu and Ni Extraction
Chemistry

Chalcocite Leach

- $\text{Cu}_2\text{S} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{CuS} + \text{CuSO}_4 + \text{FeSO}_4$
- Reaction consumes ferric ion to produce $\text{CuSO}_4$
- Reaction rate very rapid even at low temperatures. Not dependent on particle size
Chemistry

Ferric Conversion

- $2 \text{FeSO}_4 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$
- Reaction consumes oxygen, acid to produce $\text{Fe}^{3+}$ and heat
- Reaction rate dependent on $\text{Fe}^{2+}$, oxygen partial pressure
Chemistry

Pyrite Oxidation

- \( \text{FeS}_2 + 7 \text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} \rightarrow 15 \text{FeSO}_4 + 8\text{H}_2\text{SO}_4 \)
- Reaction consumes ferric ion to produce solution iron, acid and heat
- Reaction rate dependent on pyrite surface area, temperature
- 2-3% overall pyrite oxidation
MT GORDON PROCESSING PLANT
LOW TEMPERATURE AUTOCLAVE
## Costs

### Operating Costs

<table>
<thead>
<tr>
<th></th>
<th>Processing</th>
<th>Maintenance</th>
<th>Total</th>
<th>USc/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crushing</td>
<td>1.92</td>
<td>0.83</td>
<td>2.75</td>
<td>1.6</td>
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<tr>
<td>Grinding</td>
<td>9.52</td>
<td>2.26</td>
<td>11.78</td>
<td>6.9</td>
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<tr>
<td>Flotation</td>
<td>1.6</td>
<td>0.93</td>
<td>2.53</td>
<td>1.5</td>
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<tr>
<td>Leaching</td>
<td>7.91</td>
<td>4.05</td>
<td>11.96</td>
<td>7.1</td>
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<tr>
<td>Solvent Extraction</td>
<td>3.64</td>
<td>0.95</td>
<td>4.59</td>
<td>2.7</td>
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<td>Electrowinning</td>
<td>15.46</td>
<td>0.68</td>
<td>16.14</td>
<td>9.5</td>
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<tr>
<td>Tailings</td>
<td>3.52</td>
<td>0.76</td>
<td>4.28</td>
<td>2.5</td>
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<td>Laboratory</td>
<td>0.45</td>
<td>0.07</td>
<td>0.52</td>
<td>0.3</td>
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<td>Processing Management</td>
<td>2.56</td>
<td>0.69</td>
<td>3.25</td>
<td>1.9</td>
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<tr>
<td><strong>TOTAL</strong></td>
<td><strong>46.65</strong></td>
<td><strong>11.22</strong></td>
<td><strong>57.87</strong></td>
<td><strong>34.0</strong></td>
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</table>
THE SEPON COPPER PROJECT
SEPON STATISTICS

• 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).

• Resource contains 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%.

• The plant started in March 2005.

• Cash costs are estimated at 40c/lb copper
SEPON LOCALITY MAP
RECOVERY OPTIONS
Tested

SEPON RESOURCE

WHOLE ORE LEACH

WOLE ORE PRESSURE LEACH
FAILED

WHOLE ORE ATMOSPHERIC LEACH
SUCCESSFUL

FLOTATION
FAILED
MINERALOGY

QemSCAN Particle Map
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
ATMOSPHERIC LEACH CHEMISTRY

COPPER – FERRIC REACTIONS

\[ \text{CuS} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuSO}_4 + 2\text{FeSO}_4 + S_0 \]

FERRIC REGENERATION

\[ 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \frac{1}{2}\text{O}_2 = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \]
FLOTATION AND AUTOCLAVE CIRCUIT

• Flotation recovers pyrite, elemental sulfur and any copper minerals not leached in atmospheric leach, particularly the more refractory sulphides

• Autoclave Oxidation (220 C for 1 hour) converts pyrite and sulfur to basic ferric sulfate and sulfuric acid.

• Residual copper recovered in float is also leached
# MINERALOGY

<table>
<thead>
<tr>
<th>Class</th>
<th>Mineral</th>
<th>Wt %</th>
<th>Class</th>
<th>Mineral</th>
<th>Wt %</th>
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<td>Silicates</td>
<td>Quartz</td>
<td>5.3</td>
<td>Silicates</td>
<td>Quartz</td>
<td>10</td>
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<tr>
<td></td>
<td>Mica</td>
<td>5.0</td>
<td>K-Feldspar</td>
<td>&lt;0.1</td>
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<tr>
<td></td>
<td>Kaolinite</td>
<td>6.0</td>
<td>Oxide</td>
<td>Goethite</td>
<td>0</td>
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<tr>
<td>Oxides</td>
<td>Goethite</td>
<td>1.5</td>
<td>Hematite</td>
<td>5.0</td>
<td></td>
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<tr>
<td></td>
<td>Rutile</td>
<td>Tr</td>
<td>Sulphates</td>
<td>Jarosite</td>
<td>3.7</td>
</tr>
<tr>
<td>Sulphur</td>
<td>Sulphur</td>
<td>10</td>
<td>Basic Ferric</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Sulphides</td>
<td>Pyrite</td>
<td>64.2</td>
<td>Sulphur</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Covellite</td>
<td>4.4</td>
<td>Sulphides</td>
<td>Pyrite</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Enargite</td>
<td>3.0</td>
<td>Covellite</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tetrahedrite</td>
<td>0.2</td>
<td>Enargite</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chalcopyrite</td>
<td>0.1</td>
<td>Tetrahedrite</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sphalerite</td>
<td>0.2</td>
<td>Chalcopyrite</td>
<td>&lt;0.1</td>
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<tr>
<td></td>
<td>Galena</td>
<td>0.1</td>
<td></td>
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</table>
AUTOCLAVE CHEMISTRY

POX LEACH REACTIONS

\[
\begin{align*}
\text{FeS}_2 + \frac{15}{4}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} &= \frac{1}{2}\text{Fe}_2(\text{SO}_4)_3 + \frac{1}{2}\text{H}_2\text{SO}_4 \\
\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} &= 2\text{FeSO}_2\text{OH} + \text{H}_2\text{SO}_4 \\
\text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} &= \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \\
\text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} &= \text{FeOOH} + 3\text{H}_2\text{SO}_4 \\
3\text{Fe}_2(\text{SO}_4)_3 + 12\text{H}_2\text{O} + \text{K}_2\text{SO}_4 &= 2\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}_2\text{SO}_4 \\
\text{S}_6 + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O} &= \text{H}_2\text{SO}_4
\end{align*}
\]
POX RESIDUE LEACH

KEY POINTS

• Autoclave residue leach at 95 deg C,

• Leach Residence Time of 2hrs,

• Basic Ferric Sulfate re-leach before transfer to atmospheric leach.
POX RESIDUE LEACH

POX RESIDUE LEACH REACTIONS

$$2\text{FeSO}_4(\text{OH}) + \text{H}_2\text{SO}_4 = \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$$
SEPON CONCLUSIONS

• The challenge of nature at Sepon was an inexpensive source of acid for treatment of a highly leachable copper ore.

• Development of a high temperature autoclave process to make “basic ferric sulfate” that redissolves after the autoclave to replenish the reagents (acid and ferric sulfate) for leaching of copper was the metallurgical process solution.
SEPON Copper Plant

Khanong Attributes
- High grade 高品位
- Near surface 埋藏浅
- Leachable 易堆浸
- Hydro power 水电充沛
- Long life 服务年限长
- Upside 发展潜力大

Gold Plant 黄金处理厂
Crush & Grind 破矿和研磨区
Copper ROM Pad 磨机生石
Leach area 堆浸区
Electro-winning 电解车间
Oxygen plant 氧气处理厂
CCD Train CCD. 锅车
Solvent Extraction 提纯车间
Khanong open pit 卡弄氟天开采点
The BioCOP™ Process

• Thermophile bacteria oxidize sulfide minerals to metal sulfates and sulfuric acid at temperatures of 65 – 80 C.
• The BIOCOP™ flowsheet has a number of interesting features:
  – Oxygen is used for bioleaching.
  – pH control is necessary during leaching (add limestone and this limits acid by-product)
  – Arsenic may be removed in a separate step to produce a residue for disposal.
  – Copper may be recovered by SX/EW.
  – Excess acid may be used in heap leaching if appropriate.
Progress of Thermophile Copper Bioleaching

Copper dissolution (%)

Retention (days)

Oct 1999
Target set Nov 1998
Thermophile - Nov 1998
Mesophile comparison

Dew and Batty, 2003
BHP Billiton - Codelco BioCOP™ Joint Venture

• Codelco BHP Billiton joint venture announced in March 2000
• JV brings together BHP Billiton’s biotech expertise and Codelco’s SX-EW experience as world’s leading copper producer
• First project: commercial-scale plant (20 ktpa) using concentrate from Mansa Mina or Chuquicamata
• JV will develop opportunities in Chile and internationally
Site-specific economic drivers

- Electrical power cost
- Water quality and availability
- Product-to-market transport costs
- Presence of components deleterious to smelting (e.g., arsenic)
- Specific mineralogy

Dew and Batty, 2003
BioCOP™ Utilises Redundant SX/EW Capacity

- Sulfide resources
- Heap leachable resources
  - Flotation
  - Bioleach
  - Smelting/refining
  - Heap leach
  - SX/EW
  - Cathode

Dew and Batty, 2003
Prototype Plant
Bioreactors

Dew and Batty, 2003
Prototype Plant Agitator Drive

Dew and Batty, 2003
Prototype Plant
Agitator (Largest Built to Date)

Dew and Batty, 2003
BIOCOP™ Conclusions

• BioCOP™ Technology has been developed to a commercial scale and has value for treating “smelter unfriendly” primary copper ore concentrates

Dew and Batty, 2003
The Phelps Dodge Total Pressure Oxidation Process Plant at Bagdad, Arizona
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
Total Pressure Oxidation Process

Oxygen Quench Water
Wash Water

Copper Concentrate

Autoclave

S/L Separation

Washed Residue to Precious Metal Recovery

SX Loading

Raffinate acid leaching of copper or to neutralization

SX Stripping

Copper EW

Cu Cathode
Autoclaving of Copper Concentrates

$$2\text{CuFeS}_2(s) + 17/2\text{O}_2(g) + 2\text{H}_2\text{O} \xrightarrow{\Delta} 2\text{CuSO}_4(aq) + \text{Fe}_2\text{O}_3(s) + 2\text{H}_2\text{SO}_4(aq)$$
Copper Extraction Versus Time

King and Dreisinger, 1993
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
Background

- 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

Marsden et al.

JOGMEC Presentation, February 2006 – New Developments in Cu and Ni Extraction
### Process Design Criteria

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper extraction in pressure leaching</td>
<td>99.0%</td>
</tr>
<tr>
<td>Overall copper recovery</td>
<td>98.0%</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>225 C (235 C max.)</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>3,300 kPa (475 psi)</td>
</tr>
<tr>
<td>Maximum pressure</td>
<td>4,000 kPa (600 psi)</td>
</tr>
<tr>
<td>Oxygen over-pressure</td>
<td>700 kPa (100 psi)</td>
</tr>
<tr>
<td>Pressure leach vessel first compartment density</td>
<td>10% solids (by weight)</td>
</tr>
<tr>
<td>Pressure leach vessel discharge density</td>
<td>5% solids (by weight)</td>
</tr>
<tr>
<td>Leach solution composition:</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>36 g/L</td>
</tr>
<tr>
<td>Fe</td>
<td>1.5 g/L</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>55 g/L</td>
</tr>
</tbody>
</table>

Marsden et al
New Developments in Cu and Ni Extraction

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

Marsden et al
# Economics

## Key Cost Drivers

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smelting cost (long term)</td>
<td>$80-$90 per metric ton concentrate</td>
</tr>
<tr>
<td>Refining cost (long term)</td>
<td>$0.08-$0.09 per pound Cu</td>
</tr>
<tr>
<td>Acid cost (delivered)</td>
<td>$10-50 per metric ton</td>
</tr>
<tr>
<td>Freight rates (concentrate, acid, cathode)</td>
<td>Depends on local situation</td>
</tr>
<tr>
<td>Gold and silver credits</td>
<td>Depends on grade in concentrate</td>
</tr>
</tbody>
</table>

Source: Marsden et al.
## Economics

### Key Capital Cost Drivers

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate Leaching (including SX/EW)</td>
<td>$0.90 per annual lb Cu</td>
</tr>
<tr>
<td>Concentrate Leaching (excluding SX/EW)</td>
<td>&lt;$0.45 per annual lb Cu</td>
</tr>
<tr>
<td>Smelting &amp; Refining (Greenfield)</td>
<td>$1.70-2.00 per annual lb Cu</td>
</tr>
<tr>
<td>Smelting &amp; refining (Expansion)</td>
<td>&lt;$1.00 per annual lb Cu</td>
</tr>
</tbody>
</table>

Marsden et al
Total POX Conclusions

• Total Pressure Oxidation applied to copper concentrates is technically and financially feasible provided acid can be used elsewhere on the site
• Demonstration at PD Bagdad provides platform to extend to large plant size when desired
• PD has announced large autoclave facility for Morenci (235 kt/a Cu)
• Kansanshi (Zambia) is installing autoclave circuit for Total Pressure Oxidation
Chloride Processing of Chalcopyrite

- INTEC (Nippon Mining and Metals)
- Outokumpu Hydrocopper
- Sumitomo Technology (New)
Outokumpu Hydro-Copper Process

Process Uses Chlorine/Oxygen Leaching of Chalcopyrite

Copper is Precipitated as Cuprous Hydroxide

Cuprous Hydroxide is Reduced Using Hydrogen Gas

Chlorine/Caustic and Hydrogen are produced using standard Chloroalkali Cell
Chalcopyrite Leach Process

Concentrate

Oxygen

Residue containing FeO(OH) and S

Chlorine

Copper (I) Hydroxide Pptn.

NaOH

Chlor-Alkali Cell

NaCl Brine

Hydrogen Reduction of Cu

Hydrogen

Cu Metal Powder

Block Flowsheet for Outokumpu Hydrocopper Process
Chemistry of the Process (Ideal)

Chalcopyrite Leach (at least two stages of countercurrent leach)

\[ \text{CuFeS}_2 + 0.5\text{Cl}_2 + 0.75\text{O}_2 + \text{NaCl} + 0.5\text{H}_2\text{O} \]
\[ = \text{NaCuCl}_2 + \text{FeO(OH)} + \text{S} \]

Copper Precipitation

\[ \text{NaCuCl}_2 + \text{NaOH} = 2\text{NaCl} + \text{CuOH(s)} \]

Copper Reduction

\[ \text{CuOH} + 0.5 \text{H}_2(\text{g}) = \text{Cu} + \text{H}_2\text{O} \]

Chlor-Alkali Cell

\[ \text{NaCl} + \text{H}_2\text{O} = \text{NaOH} + 0.5\text{Cl}_2(\text{g}) + 0.5\text{H}_2(\text{g}) \]
Advantages

Chalcopyrite leaches well in chloride media
Good elemental sulfur yield with goethite rejection
Electrochemistry for chemical manufacture, not metal production

Disadvantages

High purity brine needed for chloralkali cell
Minor element behaviour
Copper product purity
Must reject water (evaporation)
Impurity stability?
Solution Purification

• Data from paper by Matti Hämäläinen, Olli Hyvärinen, Marika Jyrälä presented at Hydro 2003 conference in Vancouver
PURIFICATION STEPS

Chemical precipitation of impurity metals by pH increase

Cementation of silver

Removal of trace multivalent ions using ion exchange.

Hämäläinen et al
Outokumpu Hydrocopper Process including Purification Steps

Concentrate → Countercurrent Leaching

- Cu\(^{+},\ Cu^{2+}\)

CaCO\(_3\) → Cu\(^{2+}\) Precipitation

- NaOH

Cu → Silver Removal

- Hg

Na\(_2\)CO\(_3\) → Metal Precipitation

- (Zn, Pb)CO\(_3\)

HCl → Ion Exchange

Cu\(_2\)O Precipitation

- NaOH

NaCl → Chlor-alkali Electrolysis

- H\(_2\)

Reduction Melting Casting → Copper Product

- Au

Hämäläinen et al

JOGMEC Presentation, February 2006 – New Developments in Cu and Ni Extraction
Copper Quality and Process Status

12th of October 2000

Se, Te, and Bi contents of the metal were < 0.50, < 0.03, and < 0.02 ppm respectively.

Zn, and Pb contents were 0.40 and 0.35 ppm, respectively.

1 tpd Cu pilot plant running in Finland since Spring 2003

Hämäläinen et al
Sumitomo Process for Chalcopyrite

Copper concentrate → Leaching → Cu solvent extraction

Organic extracted → CuCl solution → Electrowinning → Cu metal

Raffinate → FeCl₂ solution → Purified solution → Electrowinning → Fe metal

Leaching residue → Recovery of precious metals → Concentration of precious metals → Sulfur
Sumitomo Process for Chalcopyrite

- Process announced at http://www.smm.co.jp/w_news/news_E/20050616_e.html
- Copper, iron, sulfur and precious metals are all recovered from copper concentrate
- Process is cheaper than copper smelting (capex and opex)
Nickel Hydrometallurgy

• Nickel recovery from both sulfides and laterites
• Hydrometallurgy is increasingly important for both sulfide and laterites
• Sulfides – direct leaching of nickel concentrates for nickel recovery (Pentlandite not refractory)
  – Activox (Tati)
  – Voisey Bay (Canada)
  – PLATSOL (USA)
• Laterites – direct leaching of nickel laterite ores for nickel recovery
  – HPAL (Moa Bay, Murrin Murrin, Cawse, Rio Tuba, Ravensthorpe, Goro, Ambatovy, Ramu)
Voisey Bay Process (INCO)

- Voisey Bay Ni-Co-Cu deposit discovered by Diamond Fields and sold to INCO
- Gov’t of Newfoundland requires processing of nickel values in ore to metal in province
- Ni smelter too expensive
- INCO have now developed a Hydromet process for treatment of VB concentrate
- 2004 (pilot plant starts)
- 2006 (demo plant starts)
- 2011 (commercial plant starts in Argentia, NFLD)
Voisey Bay
Nickel Process

US Patent 6,428,604, August 6, 2002
Concentrate will contain Ni, Co and Cu sulfides.
Very little precious metal content
If separate Ni/Co and Cu concentrates are floated;
Nickel concentrate (approximate)

- 15% Ni
- 0.3% Co
- <1 % Cu

For 60000 tpa Ni, cobalt production of 1200 tpa and copper
Production of less than 4000 tpa

Fine Grinding to 20 – 30 um P80.
Atmospheric Leach

Purpose is to preleach feed and to allow recycle of chlorine from electrowinning

**Pentlandite Leaching (Chlorine)**

\[ \text{Ni}_{4.5}\text{Fe}_{4.5}\text{S}_8 + 9\text{Cl}_2 = 4.5\text{NiCl}_2 + 4.5\text{FeCl}_2 + 8\text{S} \]

**Pyrrhotite Leaching (Chlorine)**

\[ \text{Fe}_7\text{S}_8 + 7\text{Cl}_2 = 7\text{FeCl}_2 + 8\text{S} \]

Oxygen also reacts with feed and acid and leaches nickel and iron – copper leaching is probably minimal

**Pentlandite Leaching (Oxygen)**

\[ \text{Ni}_{4.5}\text{Fe}_{4.5}\text{S}_8 + 4.5\text{O}_2 + 9\text{H}_2\text{SO}_4 = 4.5\text{NiSO}_4 + 4.5\text{FeSO}_4 + 8\text{S} + 9\text{H}_2\text{O} \]

**Pyrrhotite Leaching (Oxygen)**

\[ \text{Fe}_7\text{S}_8 + 3.5\text{O}_2 + 7\text{H}_2\text{SO}_4 = 7\text{FeSO}_4 + 8\text{S} + 7\text{H}_2\text{O} \]
Pressure Leach (150 C)

Purpose is to finish leach of feed using pressure oxygen and form hematite solids from solution.

**Pentlandite Leaching (Oxygen + Sulfuric Acid)**

\[ \text{Ni}_{4.5}\text{Fe}_{4.5}\text{S}_8 + 4.5\text{O}_2 + 9\text{H}_2\text{SO}_4 = 4.5\text{NiSO}_4 + 4.5\text{FeSO}_4 + 8\text{S} + 9\text{H}_2\text{O} \]

**Pentlandite Leaching (Oxygen + Sulfuric Acid + Hydrochloric Acid)**

\[ \text{FeCl}_2 + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + 2\text{HCl} \]

\[ \text{Ni}_{4.5}\text{Fe}_{4.5}\text{S}_8 + 4.5\text{O}_2 + 4.5\text{H}_2\text{SO}_4 + 9\text{HCl} = 4.5\text{NiCl}_2 + 4.5\text{FeSO}_4 + 8\text{S} + 9\text{H}_2\text{O} \]

**Pyrrhotite Leaching (Oxygen + Sulfuric Acid)**

\[ \text{Fe}_7\text{S}_8 + 3.5\text{O}_2 + 7\text{H}_2\text{SO}_4 = 7\text{FeSO}_4 + 8\text{S} + 7\text{H}_2\text{O} \]

**Chalcopyrite Leaching (Oxygen + Sulfuric Acid)**

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

**Ferrous Sulfate Oxidation**

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

**Ferric Sulfate Hydrolysis to Hematite**

\[ \text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \]

**Ferric Sulfate Hydrolysis to Hydronium Jarosite**

\[ 4\text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} = \text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6 + 3\text{H}_2\text{SO}_4 \]

**Elemental Sulfur Oxidation**

\[ \text{S} + 1.5\text{O}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 \]
Pressure Leach Notes

Presence of chloride in solution reduces sulfur oxidation to sulfate
Result is high yield of elemental sulfur

Pressure leach solution will contain
- FeSO$_4$
- Fe$_2$(SO$_4$)$_3$
- NiSO$_4$
- NiCl$_2$
- H$_2$SO$_4$
- Minor elements, Co, Zn, Mn, Mg, Ca, As, Sb, Se, Te, etc.

Pressure leach solids will contain
- S + Unreacted Sulfides
- Fe$_2$O$_3$
- Hyd-Jarosite
- Gangue + Minor species
Liquid-Solid Separation
• Rejects Barren Solids to Waste

Copper Removal
• Either by SX/EW or by Direct Precipitation with NaSH

Neutralization/Iron Precipitation
• Limestone Neutralization with Oxidation to Reject Gypsum and Goethite

Solution Purification
• D2EHPA Extraction of Zn/Mn/Cu(residual)/Ca from Solution – strip with HCl to reject waste solution with these elements.

Cobalt Recovery
• Cobalt SX with Cyanex 272
Nickel Electrowinning

Cathode Processes (Ni starter sheet or Ti blank)
\[ \text{NiCl}_2 + 2e = \text{Ni} + 2\text{Cl}^- \]
\[ \text{NiSO}_4 + 2e = \text{Ni} + \text{SO}_4^{2-} \]

Anode Processes (DSA Anode)
\[ 2\text{Cl}^- = \text{Cl}_2(g) + 2e \]
\[ \text{H}_2\text{O} = \frac{1}{2} \text{O}_2(g) + 2\text{H}^+ + 2e \]

Overall
\[ \text{NiCl}_2 = \text{Ni} + \text{Cl}_2(g) \]
\[ \text{NiSO}_4 + \text{H}_2\text{O} = \text{Ni} + \text{H}_2\text{SO}_4 + \frac{1}{2} \text{O}_2(g) \]
Voisey Bay Conclusions

• VB Process involves control of sulfur oxidation by addition of chloride to autoclave solution
• Solution purification steps suitable to control Cu, Fe, Zn/Mn/Ca, Co
• Major innovation in direct electrowinning from high strength Ni-SO$_4$-Cl solution
  – Anode design and coating
  – Additives for EW?
• Extensive program of pilot – demo – commercial installation
• Looks like a promising process for replacement of Ni smelters for sulfide concentrate treatment
THE PLATSOL® PROCESS
Introduction

• The NorthMet deposit (Minnesota) discovered in the 1970’s. Now owned by PolyMet
• Large, low grade polymetallic deposit (Cu, Ni, Co, Au, Pt, Pd)
• > 900 million tons @ >0.90 Cu Equivalent grade at a 0.15% Cu cut off grade.
• **Challenge of Nature**: Must recover all metals of value for the deposit to be economically viable.
• **Solution**: Develop a new process (PLATSOL) that unlocks the value from the deposit.
Introduction

• PLATSOL™ Process
  – Simple process for one-step dissolution of base and precious metals
  – Invented at Lakefield Research
  – Tested via Batch and Continuous Autoclave Programs at Lakefield
  – High levels of base (+95-99%) and precious metals (+95%) recovery
Mesabi Iron Range – NE Minnesota
Cleveland Cliffs Erie Plant – Treated 100,000 tpd of iron ore – now owned by PolyMet Mining for NorthMet Processing
PLATSOL™ Process

One Step Treatment to Dissolve Base (Cu, Ni, Co) and Precious Metals (Au, Pt, Pd, Ag, Rh, Ir, Os, Ru)

Simple, Conventional Equipment (common use in gold and copper industry)

Autoclave (high temperature reactor 428 F, 220 C) for “Pressure Oxidation” of the Ore using Oxygen (from air) is Central. Salt added.

Autoclave Vent is Mainly Steam and Excess Oxygen.

Acid is Produced by Reaction between Oxygen and Sulfur. This Acid is Neutralized with Limestone to Produce Synthetic Gypsum or Wallboard. Acid is not released from the process.

Well Established Processes for Base and Precious Metal Recovery
PLATSOL™ Principles

Under PLATSOL leaching conditions all value metals are efficiently dissolved

Addition of Chloride to High Temperature Pressure Oxidation to Promote Leaching of Precious and Base Metals.

PGM’s, Copper, Nickel and Cobalt can then be selectively extracted

The following slides show the chemistry of PLATSOL
PLATSOL™ Principles

Chalcopyrite Oxidation/Iron Hydrolysis:
\[ \text{CuFeS}_2 + 17/4 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{CuSO}_4 + 1/2 \text{Fe}_2\text{O}_3 + \text{H}_2\text{SO}_4 \]

Pyrite Oxidation:
\[ \text{FeS}_2 + 15/4 \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 1/2 \text{Fe}_2\text{O}_3 + 2\text{H}_2\text{SO}_4 \]

Pyrrhotite Oxidation:
\[ \text{FeS} + 9/4 \text{O}_2 + \text{H}_2\text{O} \rightarrow 1/2 \text{Fe}_2\text{O}_3 + \text{H}_2\text{SO}_4 \]

Nickel Sulfide Oxidation:
\[ \text{NiS} + 2\text{O}_2 \rightarrow \text{NiSO}_4 \]

Gold Oxidation/Chlorocomplex Formation:
\[ \text{Au} + 3/4 \text{O}_2 + 3/2 \text{H}_2\text{SO}_4 + 4\text{NaCl} \rightarrow \text{NaAuCl}_4 + 3/2 \text{Na}_2\text{SO}_4 + 3/2 \text{H}_2\text{O} \]

Platinum Oxidation/Chlorocomplex Formation:
\[ \text{Pt} + \text{O}_2 + 2\text{H}_2\text{SO}_4 + 6\text{NaCl} \rightarrow \text{Na}_2\text{PtCl}_6 + 2\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \]

Palladium Oxidation/Chlorocomplex Formation:
\[ \text{Pd} + 1/2 \text{O}_2 + \text{H}_2\text{SO}_4 + 4\text{NaCl} \rightarrow \text{Na}_2\text{PdCl}_4 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \]
PLATSOL™ Principles

Eh – pH Diagram for the Au-Cl system at 25 C.
[Au] = 0.00001 M. [Cl] = 0.2 M.
PLATSOL™ Principles

Eh – pH Diagram for the Pd-Cl system at 25 C.
[Pd] = 0.00001 M. [Cl] = 0.2 M.
PLATSOL™ Principles

Eh – pH Diagram for the Pd-Cl system at 25 C.

\[ [\text{Pd}] = 0.00001 \text{ M. } [\text{Cl}] = 0.2 \text{ M.} \]
### Bulk Flotation

<table>
<thead>
<tr>
<th>Analysis (% or g/t)</th>
<th>Cu</th>
<th>Ni</th>
<th>Co</th>
<th>Fe</th>
<th>S(^2)</th>
<th>Au</th>
<th>Pt</th>
<th>Pd</th>
<th>Total PGMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore</td>
<td>0.43</td>
<td>0.12</td>
<td>0.009</td>
<td>10.8</td>
<td>1.01</td>
<td>0.06</td>
<td>0.08</td>
<td>0.37</td>
<td>0.59</td>
</tr>
<tr>
<td>Concentrate</td>
<td>15.5</td>
<td>3.69</td>
<td>0.15</td>
<td>28.7</td>
<td>25.6</td>
<td>2.80</td>
<td>2.49</td>
<td>11.1</td>
<td>16.7</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>93.7</td>
<td>77.1</td>
<td>46.4</td>
<td></td>
<td></td>
<td>76.6</td>
<td>76.4</td>
<td>75.8</td>
<td></td>
</tr>
</tbody>
</table>
### Pressure Oxidation: Conventional and PLATSOL Metal Extractions (220 C)

<table>
<thead>
<tr>
<th>Element</th>
<th>Conventional</th>
<th>PLATSOL**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>99.3</td>
<td>99.6</td>
</tr>
<tr>
<td>Ni</td>
<td>95.9</td>
<td>98.9</td>
</tr>
<tr>
<td>Co</td>
<td>&gt;92</td>
<td>96</td>
</tr>
<tr>
<td>Fe</td>
<td>11.5</td>
<td>11.5</td>
</tr>
<tr>
<td>S</td>
<td>91.5</td>
<td>91.5</td>
</tr>
<tr>
<td>Pt</td>
<td>~0</td>
<td>96</td>
</tr>
<tr>
<td>Pd</td>
<td>61.1</td>
<td>94.6</td>
</tr>
<tr>
<td>Au</td>
<td>~0</td>
<td>89.4</td>
</tr>
</tbody>
</table>

** ACTUAL PILOT PLANT RESULTS FROM LAKEFIELD
PLATSOL™ Principles

• Precious Metals Recovered by Precipitation with NaSH or MeS (CuS)
• Cu Recovered by Solvent Extraction and Electrowinning
• Ni/Co Recovered as Mixed Hydroxide using Magnesium Oxide Precipitation
Open Pit Mine

Rail

Crushing
Grinding
Flotation

Tailings Basin

Lined Cells

Autoclave

Hydrometallurgical Processing

SX/EW

NICKEL/COBALT 7,875 tons/year metal in precipitate

PLATINUM, PALLADIUM, GOLD 120,900 oz/year metal in precipitate

COPPER CATHODE 33,000 tons/year high purity metal

Waste Stockpile

27,500 tpd waste

670 tpd concentrate
PLATSOL Conclusions

- The Project: NorthMet is an exciting project with potential for a long life, profitable mine and processing facility
- The Process: The PLATSOL™ process has been developed to unlock the metals of value from NorthMet. Simple concept with exceptional results
Nickel Laterite Hydrometallurgy

- HPAL is dominant with mixed sulfide, mixed hydroxide or direct metal recovery
- Caron is limited by energy cost for reduction
- Enhanced Pressure Acid Leaching (EPAL), atmospheric leaching for saprolites combined with HPAL for limonites – under construction at Ravensthorpe
- Great deal of interest in chloride based leaching processes for laterites (with HCl regeneration from MgCl₂). BHP Billiton, Jaguar Nickel, Nichromet
- Heap Leaching of Laterites (and Sulfides) is progressing (European Nickel and Titan Resources)
European Nickel – Caldag, Turkey

Test Heap

Flowsheet
Thank You!

Any Questions?