Hydrometallurgical Processing of Polymetallic Nodules from the Clarion Clipperton Zone (CCZ)

3 September 2018
Background

David Dreisinger/Dreisinger Consulting Inc.
University of British Columbia Chair in Hydrometallurgy
+300 papers, 21 US patents granted
Process development, process improvement, education and training
<table>
<thead>
<tr>
<th>Project Name</th>
<th>Details</th>
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<tbody>
<tr>
<td><strong>Mt. Gordon Copper Process, Australia</strong></td>
<td>50,000 tpa Cu by leach-SX-EW</td>
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<td>US6537440, Processing Copper Sulphide Ores, 2003-03-25, Richmond, Geoffrey, Dreisinger, David B.</td>
</tr>
</tbody>
</table>

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| **Sepon Copper Process, Laos**               | 90,000 tpa Cu by Leach-SX-EW                                            |
|                                              | US7799295, Ore Leach Method with Aqueous Sulfuric Acid containing Ferric Ions, 2010-09-21, Dreisinger, David B, Pratt, Graham, Baxter, Kenneth Gordon, OZ Minerals Limited |

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| **Boleo Project, Mexico**                    | 60,000 tpa Cu, 2,000 tpa Co, 8,000 tpa Zn and MnCO₃ Potential          |

Boleo-Korea Herald Feb 6, 2015
Current Development Activities

• Hydrometallurgical Lead Refinery Design, (LeadFX, Australia)

• Starved Acid Leaching Technology (SALT) for nickel laterites (InCoR Technologies)

• The Search Minerals Direct Extraction Process for Rare Earth Recovery (Search Minerals, Canada)

• Hydrometallurgical processing technology for manganese nodules (UK Seabed Resources)
Historical Processing Routes for Mn Nodules
(3 metals: Ni, Co, Cu)

Ammoniacal Systems
- Gas reduction and ammoniacal leach (3 metal)
- Cuprion ammoniacal leach (3 metal with option for Mn)
- High-temperature ammonia leach

Chloride Systems
- Reduction and HCl leach (3 metal)
- HCl reduction roast and acid leach
- Segregation roast
- Molten salt chlorination

Sulphate Systems
- High temperature and high pressure H₂SO₄ leach (4 metal)
- Smelting and H₂SO₄ leach (4 metal)
- H₂SO₄ reduction leach
- Reduction roast and H₂SO₄ leach
- Sulphate roast

Gas Reduction and Ammoniacal Leach

- Adaptation of the Caron process that is used for nickel laterite processing
- Nodule ore is dried and then roasted at 625° C using a carbon monoxide rich producer gas.
- Manganese dioxide minerals to manganese oxide and copper, nickel and cobalt leachable
- Roaster calcine is leached in an ammonia/ammonium carbonate solution Cu, Ni, Co.
- Mn stays as manganese carbonate in the residue.
- Cu – Cu Solvent extraction and Electrowinning
- Ni – Ni Solvent extraction and electrowinning
- Co – Co sulfide precipitate
- Ammonia and carbon dioxide recovered by steam stripping
- High energy use for drying and reduction
- Caron plants in Brazil, Australia and Cuba. Only Cuba remains operating

Queensland Nickel Refinery (Yabulu)

High-temperature and High-pressure Sulfuric Acid Leach

- Same technology as used in nickel laterites (i.e. High Pressure Acid Leach (HPAL))
- Plants have been built in Cuba (1960’s) and then Australasia, Asia, Africa and Middle East
- High T (245˚ to 270˚ C) and High P (4000-5000 kPa)
- Nodules extracted to form Ni, Co, Cu in solution
- Manganese is converted to a water soluble manganese sulphate salt.
- The copper and nickel are recovered from solution using solvent extraction and electrowinning with pH adjustment by ammonia addition.
- Cobalt is recovered as a cobalt sulphide by addition of a source of sulphide to the nickel solvent extraction raffinate.
- Ammonia is recovered (and presumably manganese is precipitated) by effluent treatment with lime.

Reduction and Hydrochloric Acid Leach

- Nodules are dried and leached with hydrochloric acid (HCl)
- Chlorine is recovered and used to regenerate HCl
- Metal chloride salts are recovered
- Cu, Ni by solvent extraction and electrowinning
- Co by solvent extraction and precipitation
- Manganese by manganese chloride crystallization, dehydration and molten salt electrowinning to make Mn metal.
- High energy cost for drying of nodules and evaporation/crystallization of manganese chloride
- Novel manganese reduction technology for manganese chloride to manganese metal
- Melting point for Mn is 1246°C – high temperature molten salt – novel

Nikkelverk Ni/Co/PGM Refinery (Norway)

http://krsbib.no/aktivitet/hva-skjedde-pa-nikkelverket-i-1975/
Smelting and Sulfuric Acid Leach

- Nodules are ground and dried and then electric furnace smelted (1425° C)
- Alloy of Cu-Ni-Co-Mn (minor) is recovered
- Slag contains Fe-Mn – fed to another furnace for reduction to ferromanganese
- Alloy is smelted with oxygen and gypsum (CaO for slag and S for matte formation)
- Product is a Cu-Ni-Co matte (metal sulfides)
- Matte pressure leached to redissolve the metals
- Cu – SX-EW, Ni – SX-EW and Co (Sulphide precipitation)
- Ammonia used for pH adjustment with liming of barren solutions to recover ammonia
- High specific energy use
- Process requires multiple high temperature steps (3) plus extensive use of hydrometallurgy
Cuprion

- The Cuprion process is a development of the Kennecott Copper Corporation (KCC) and is often referred to as the KCC – Cuprion Process.
- The process involves a reductive ammonia-ammonium carbonate leach of the manganese nodules.
- The reducing gas is a producer gas containing carbon monoxide, hydrogen and small amounts of carbon dioxide, oxygen and nitrogen.
- The carbon monoxide (and hydrogen) reduce cupric ion (hence the name Cuprion for the process) to the cuprous state which is stabilized by the ammonia-ammonium carbonate solution composition.
- The cuprous ion then reacts with manganese dioxide to form the manganous ion (Mn2+) which promptly precipitates as manganese carbonate.
- The nickel, copper and cobalt contained in the manganese nodules is leached into solution as the manganese dioxide is converted to manganese carbonate.
Cuprion Process Flow

- Manganese dioxide reduction
  \[ \text{MnO}_2 + 2\text{Cu(NH}_3\text{)}_2^+ + 2(\text{NH}_4\text{)}_2\text{CO}_3 = \text{MnCO}_3 + 2\text{Cu(NH}_3\text{)}_4^{2+} + \text{CO}_3^{2-} + 2\text{H}_2\text{O} \]

- Carbon monoxide reduction of cupric to cuprous
  \[ 2\text{Cu(NH}_3\text{)}_4^{2+} + \text{CO} + + \text{CO}_3^{2-} + 2\text{H}_2\text{O} = 2\text{Cu(NH}_3\text{)}_2^+ + 2(\text{NH}_4\text{)}_2\text{CO}_3 \]

- Net overall reaction
  \[ \text{MnO}_2 + \text{CO} = \text{MnCO}_3 \]

- The leaching of the base metals results in the dissolution of the ammines of copper, nickel and cobalt.
  \[ \text{CuO} + (\text{NH}_4\text{)}_2\text{CO}_3 + 2\text{NH}_3 = \text{Cu(NH}_3\text{)}_4\text{CO}_3 + \text{H}_2\text{O} \]
  \[ \text{CoO} + (\text{NH}_4\text{)}_2\text{CO}_3 + 3\text{NH}_3 = \text{Co(NH}_3\text{)}_5\text{CO}_3 + \text{H}_2\text{O} \]
  \[ \text{NiO} + (\text{NH}_4\text{)}_2\text{CO}_3 + 4\text{NH}_3 = \text{Ni(NH}_3\text{)}_6\text{CO}_3 + \text{H}_2\text{O} \]
• The mixed ammine leach solution is then treated by solvent extraction to recover copper and nickel metal.

• Cobalt (oxidized to +3 state after leaching) and molybdenum are not extracted during the solvent extraction process.

• Cobalt and molybdenum are recovered as a mixed byproduct from the steam – stripping and recovery of ammonia and carbon dioxide.
Cuprion Features

- Metals are disseminated in the oxide matrix and not amenable to beneficiation
- Nodules are very porous (50% to 60%). 30% - 40% free moisture + 10% to 15% bound water.
- Any process that requires drying requires substantial energy input
- Kennecott Cuprion Process with following features:
  - Ambient temperature,
  - Low pressure,
  - Operable in the presence of sea water,
  - Inexpensive or recyclable reagents,
  - Low energy consumption,
  - High and selective recovery of nickel, copper, cobalt and molybdenum,
  - Non-corrosive to materials of construction,
  - Low toxicity reagents, and
  - Acceptable environmental impact.

Manganese from Cuprion

- Primary Cuprion Residue is Manganese Carbonate (high grade)
- Electrolytic Manganese Metal (EMM) is commonly produced from manganese carbonate ores
- Processing will allow higher overall recovery of other metals (Cu, Ni, Co, Mo) and potentially other minor metals
Manganese Recovery Options

• Manganese products (examples)
  – Ferro-alloys
  – Electrolytic Manganese Metal (EMM)
  – Electrolytic Manganese Dioxide (EMD)
  – Manganese Salts (eg. MnSO$_4$·H$_2$O)
    • Now important for lithium ion battery formulations
EMM Chemistry

- Manganese leaching
  \[ \text{MnCO}_3 + \text{H}_2\text{SO}_4 = \text{MnSO}_4 + \text{H}_2\text{O} + \text{CO}_2(\text{g}) \]
- Solution purification
  \[ \text{MeSO}_4 + (\text{NH}_4)_2\text{S} = \text{MS} + (\text{NH}_4)_2\text{SO}_4, \text{ where Me=Cu, Ni, Co, Zn, Cd} \]
- Manganese electrowinning
  \[ \text{MnSO}_4 + \text{H}_2\text{O} = \text{Mn} + \frac{1}{2} \text{O}_2(\text{g}) + \text{H}_2\text{SO}_4 \]
EMM processing enhances metal recovery
# SGS Minerals: Benchscale Amenability Testing

## Overall Leach Extractions

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<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Ni</th>
<th>Co</th>
<th>Mo</th>
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<tr>
<td><strong>Reduction Leaching</strong></td>
<td>63.9%</td>
<td>97.9%</td>
<td>81.8%</td>
<td>98.4%</td>
</tr>
<tr>
<td><strong>Acid Leaching</strong></td>
<td>34.8%</td>
<td>1.9%</td>
<td>14.5%</td>
<td>0.4%</td>
</tr>
<tr>
<td><strong>Overall Recovery</strong></td>
<td>98.7%</td>
<td>99.8%</td>
<td>96.3%</td>
<td>98.8%</td>
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*Note: Acid leach recoveries are based on input nodules*
Bench and Pilot Plant Scale Development of an Improved Cuprion Process

Recent experience with developing test programs (bench scale and pilot scale) for metallurgical process development.

- **El Boleo – Mexico** (Baja Mining, Now KORES) - Operating
- **Sepon Copper – Lao** (Oxiana) – Operating
- **NorthMet – USA** (PolyMet Mining) - Permitting
- **Malku Khotu – Bolivia** (South American Silver) – Arbitration
- **Foxtrot – Canada** (Search Minerals) - Development
- **Paroo Station Lead Refinery – Australia** (LeadFX) – Development
Conclusions

- Manganese nodule processing is feasible based on previous technology experience
- Improvements in all aspects of the Cuprion process are likely possible based on technology advances being incorporated in recent projects
- Manganese recovery from Cuprion residues as EMM or high purity manganese salts is likely feasible and allows for increased overall recovery of Cu, Ni, Co, Mo and potential by-product recovery

Cuprion process appears to be a leading candidate for treatment of polymetallic nodules