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

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Consultant to UK Seabed Resources

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

Dreisinger Consulting Previous Projects

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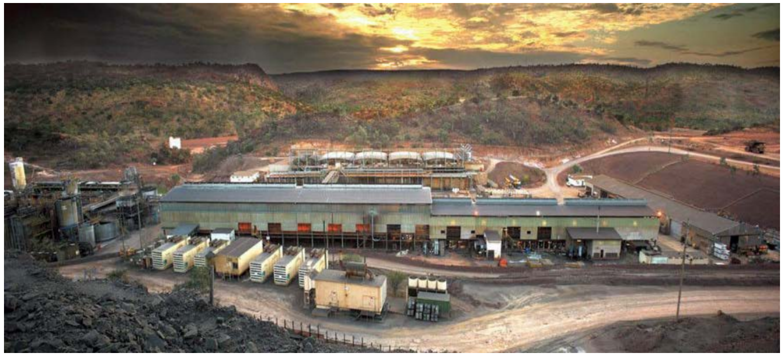
Mt. Gordon Copper Process, Australia

50,000 tpa Cu by leach-SX-EW

US6537440, Processing Copper Sulphide Ores, 2003-03-25, Richmond, Geoffrey, Dreisinger, David B.



Dreisinger Consulting Inc

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 .

Dreisinger Consulting Inc

Boleo Project, Mexico

60,000 tpa Cu, 2,000 tpa Co, 8,000 tpa Zn and $MnCO_3$ Potential

Dreisinger, D.B., Murray, W., Norton, E., Baxter, K., Holmes, M. and Molnar, R., “The Boleo Copper-Cobalt-Zinc-Manganese Project”, Canadian Metallurgical Quarterly (2008), 47(3), 357-367.

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)

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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 H_2SO_4 leach (4 metal)
- Smelting and H_2SO_4 leach (4 metal)
- H_2SO_4 reduction leach
- Reduction roast and H_2SO_4 leach
- Sulphate roast

Dames and Moore, and E.I.C. Corporation (1977), "Description of Manganese Nodule Processing Activities for Environmental Studies, Vol. III. Processing Systems Technical Analysis. U.S. Dep. Commerce – NOAA, Office of Marine Minerals, Rockville, MD, 1977, 540 pp.; NTIS PB 274912(set).

Gas Reduction and Ammoniacal Leach

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- 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)

https://www.northqueenslandregister.com.au/story/3553474/yabulu-waiting-game-continues/

High-temperature and High-pressure Sulfuric Acid Leach

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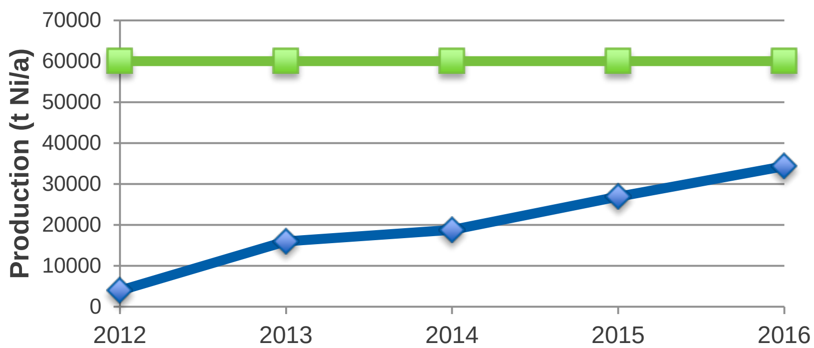
- Same technology as used in nickel laterites (i.e. High Pressure Acid Leach (HPAL))
- Plants have been built in Cuba (1960's) and then Australasia, Asia, Africa and Middle East
- High T (245˚ to 270˚ C) and High P (4000-5000 kPa)
- Nodules extracted to form Ni, Co, Cu in solution
- Manganese is converted 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.

Goro Nickel Plant (New Caledonia)

Goro Nickel Plant Ramp Up



https://nanthavictor.com/2018/04/26/future-of-vales-nickel-operation-in-newcaledonia/

Reduction and Hydrochloric Acid Leach

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- 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

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- 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

Atlantic Copper Smelter,
(Huelva, Spain)

Atlantic Copper http://www.atlantic-copper.es

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 Pilot Plant
(Kennecott)

Cuprion Process Flow

- Manganese dioxide reduction

  $MnO_2 + 2Cu(NH_3)_2^+ + 2(NH_4)_2CO_3 = MnCO_3 + 2Cu(NH_3)_4^{2+} + CO_3^{2-} + 2H_2O$

- Carbon monoxide reduction of cupric to cuprous

  $2Cu(NH_3)_4^{2+} + CO + + CO_3^{2-} + 2H_2O = 2Cu(NH_3)_2^+ + 2(NH_4)_2CO_3$

- Net overall reaction

  $MnO_2 + CO = MnCO_3$

- The leaching of the base metals results in the dissolution of the ammines of copper, nickel and cobalt.

  $CuO + (NH_4)_2CO_3 + 2NH_3 = Cu(NH_3)_4CO_3 + H_2O$

  $CoO + (NH_4)_2CO_3 + 3NH_3 = Co(NH_3)_5CO_3 + H_2O$

  $NiO + (NH_4)_2CO_3 + 4NH_3 = Ni(NH_3)_6CO_3 + H_2O$

Cuprion Process/Metal Recovery

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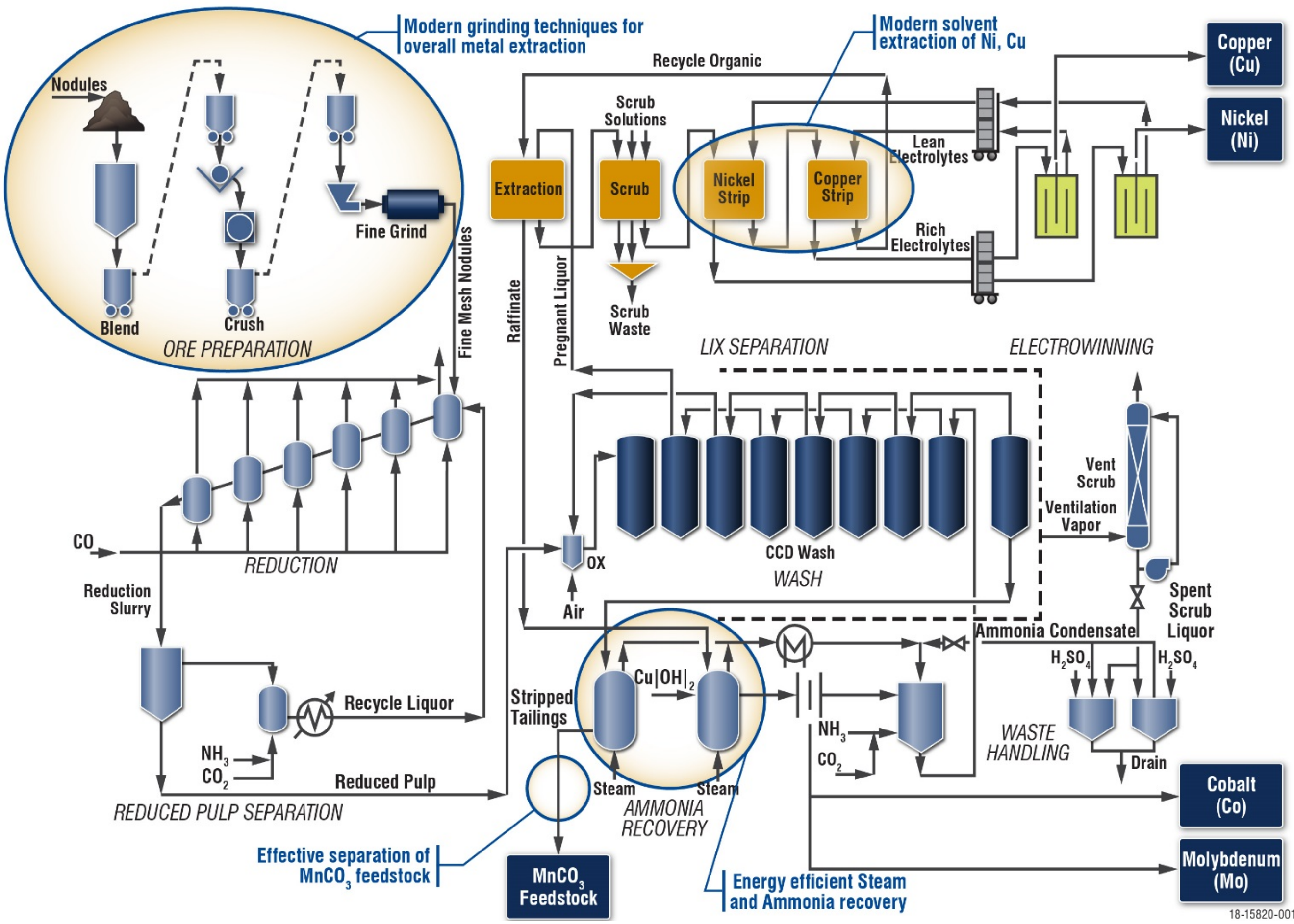
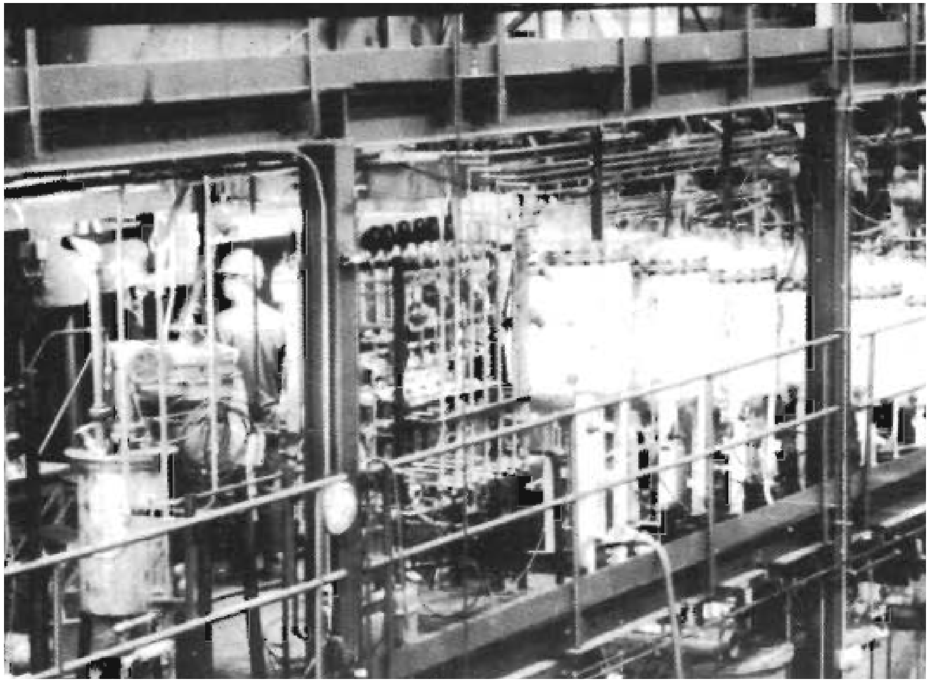


- The mixed ammine leach solution is then treated by solvent extraction to recover copper and nickel metal.
- Cobalt (oxidized to +3 state after leaching) and molybdenum are not extracted during the solvent extraction process.
- Cobalt and molybdenum are recovered as a mixed byproduct from the steam – 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.*



Cuprion Pilot Plant (Kennecott)

Agarwal, J.C., Barner, H.E., Beecher, N., Davies, D.S., Kust, R.N. (1979), "Kennecott Process for Recovery of Copper, Nickel, Cobalt and Molybdenum from Ocean Nodules", Min. Eng. (N.Y.), 31, 1704-1709.

Manganese from Cuprion

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- 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

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- Manganese products (examples)
  - Ferro-alloys
  - Electrolytic Manganese Metal (EMM)
  - Electrolytic Manganese Dioxide (EMD)
  - Manganese Salts (eg. $MnSO_4.H_2O$)
    - Now important for lithium ion battery formulations

EMM Chemistry

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- Manganese leaching

  $MnCO_3 + H_2SO_4 = MnSO_4 + H_2O + CO_2(g)$

- Solution purification

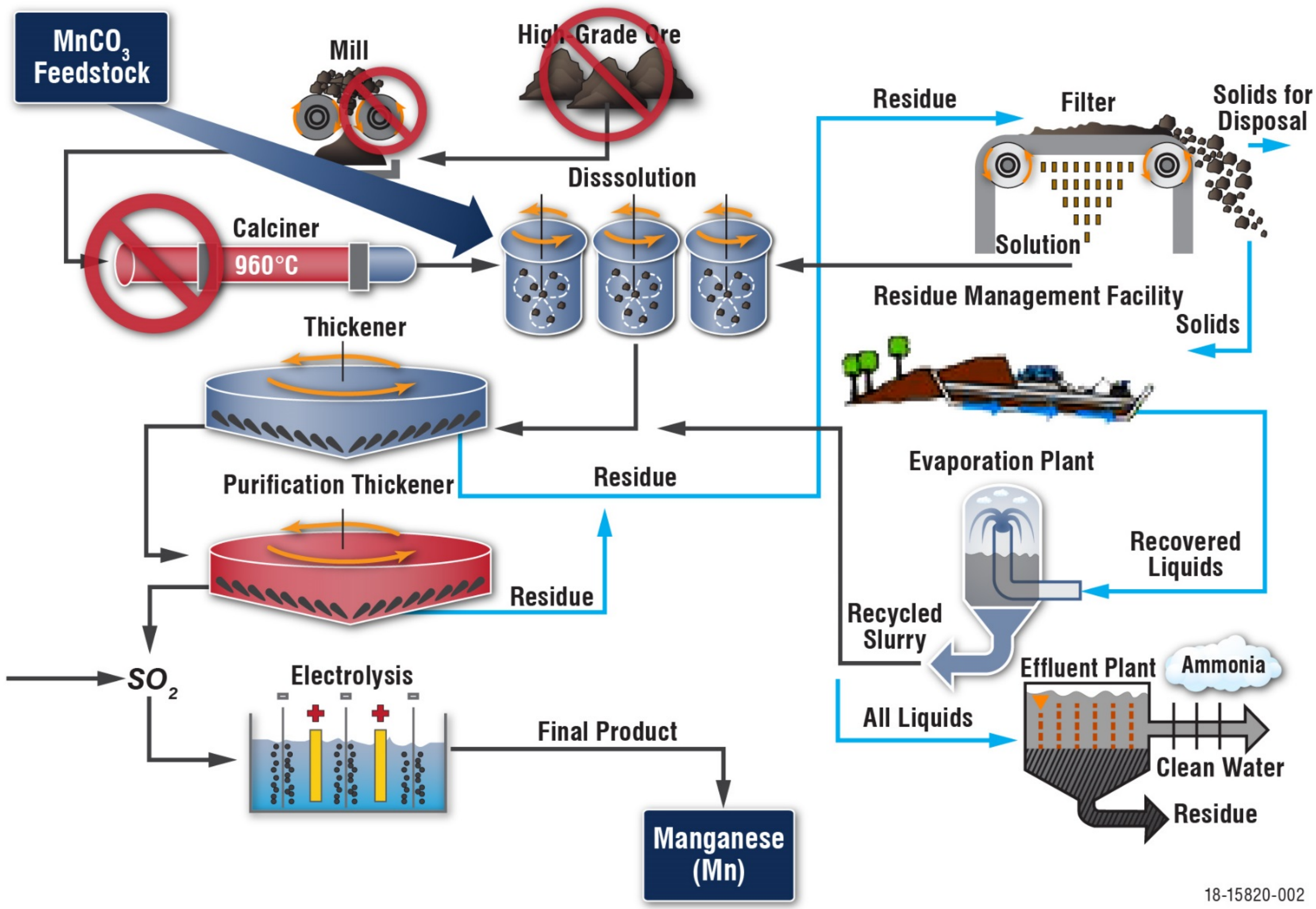
  $MeSO_4 + (NH_4)_2S = MS + (NH_4)_2SO_4$, where Me=Cu, Ni, Co, Zn, Cd

- Manganese electrowinning

  $MnSO_4 + H_2O = Mn + ½ O_2(g) + H_2SO_4$

Manganese Metal Processing
(Manganese Dioxide Ore)

UK Seabed Resources



EMM processing enhances metal recovery

SGS Minerals: Benchscale Amenability Testing

Overall Leach Extractions

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	Cu	Ni	Co	Mo
Reduction Leaching	63.9%	97.9%	81.8%	98.4%
Acid Leaching	34.8%	1.9%	14.5%	0.4%
Overall Recovery	98.7%	99.8%	96.3%	98.8%

Note: Acid leach recoveries are based on input nodules

Bench and Pilot Plant Scale Development of an Improved Cuprion Process

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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

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- 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

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