



Hydrometallurgical Process Development for Complex Ores and Concentrates

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Introduction

- Traditionally, copper, nickel, cobalt, zinc and lead recovery from sulfide deposits by, mining, flotation of concentrates and finally smelting/refining of the concentrates through to final products
- But...
- Complex fine grained ores – poor for flotation, suited to leaching
- Pyrometallurgy expensive, environment (gases and dusts), poor by-product recovery versus hydrometallurgy with lower cost, no dust or gases, excellent by-product recovery.



Introduction

- Great strides in;
 - Copper – Leach, SX-EW, Concentrate Leach
 - Nickel/cobalt – Sulfide and laterite leaching
 - Zinc – Skorpion Leach SX-EW, Concentrate Leaching
 - Lead – Still Waiting!



Mineral Processing Hydrometallurgy Pyrometallurgy

Complex ores
Loss of values in tails



High capital cost
Environmental constraints
Loss of byproducts in slags
and residues

Mineral Processing **Hydrometallurgy** Pyrometallurgy



Hydrometallurgy Process Development

- Problem Driven or Solution Driven?
- Problem Driven – deposit that can not be treated by conventional technology
- Solution Driven – develop general solution to problem and then seek application



Solution Driven Examples

- Copper Concentrate Treatment
- +50 Processes developed to replace smelters
- Very few have achieved commercial success
- Currently;
 - Total Pressure Oxidation
 - Anglo American Corporation – Univ. of B.C./Phelps Dodge Process
 - CESL Process
 - BIO COP Process
 - GALVANOX™



GALVANOX CHEMISTRY

- GALVANOX takes advantage of the galvanic effect between chalcopryrite and pyrite.
- Chalcopryrite is a semiconductor, and therefore corrodes electrochemically in oxidizing solutions.
- In ferric sulphate media, the overall leaching reaction is as follows:

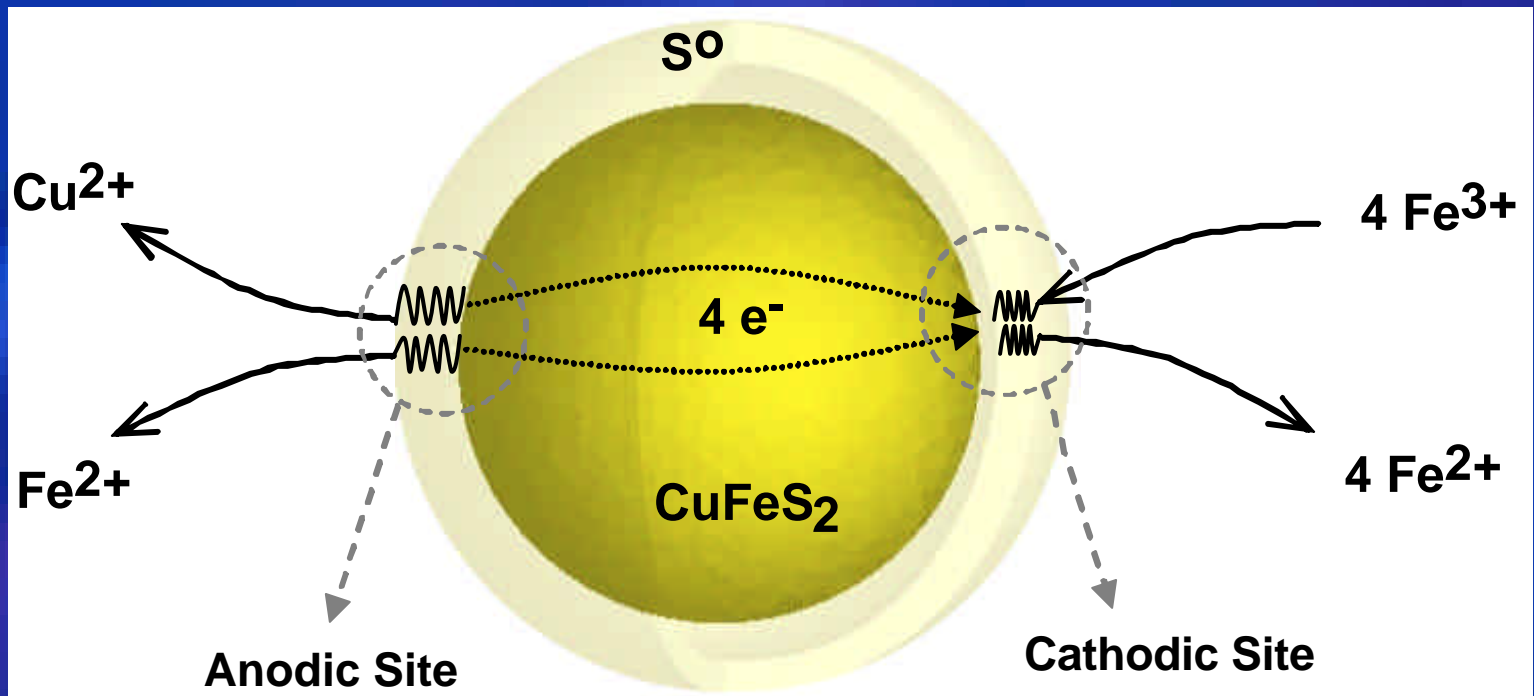


- This reaction may be represented as a combination of anodic and cathodic half-cell reactions:



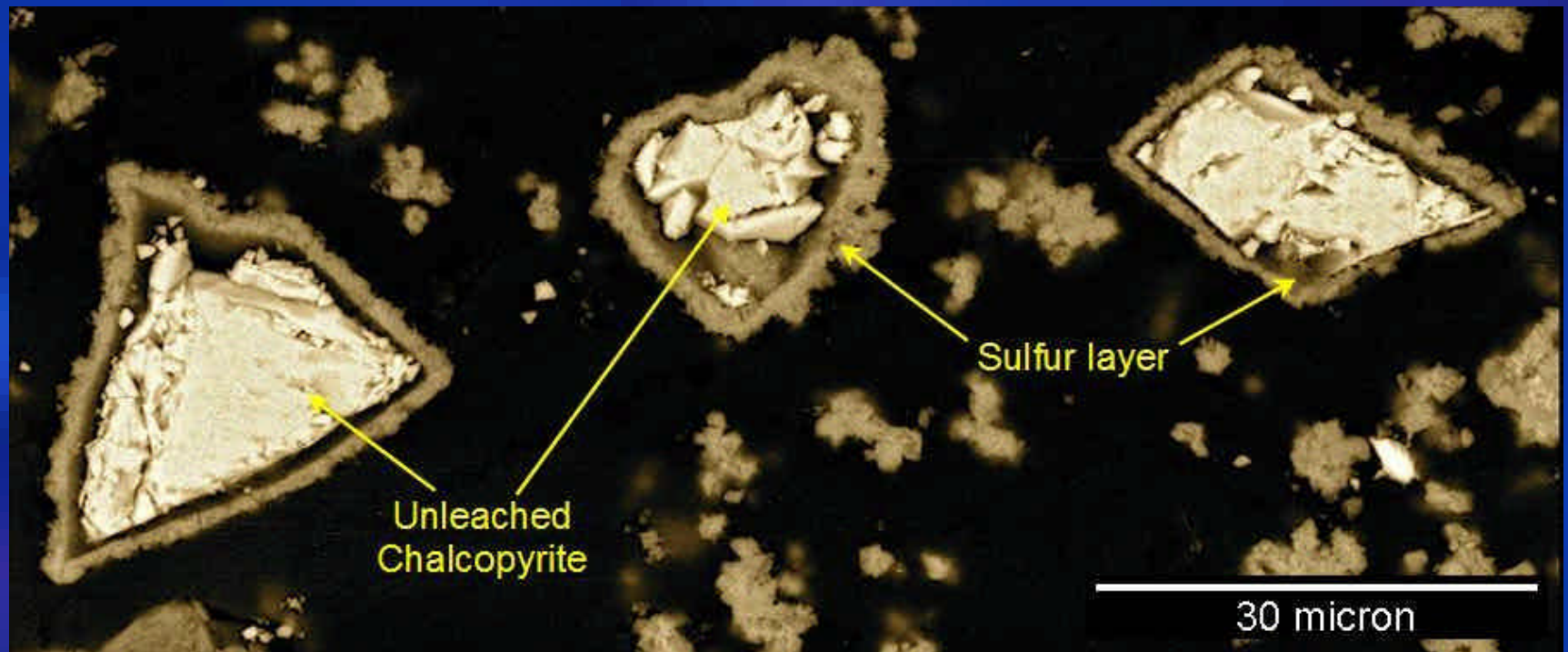


UNASSISTED CHALCOPYRITE LEACHING





UNASSISTED CHALCOPYRITE LEACHING





GALVANOX CHEMISTRY

- Typically, chalcopryrite surfaces are passivated (i.e., they become resistant to electrochemical breakdown) in ferric sulfate solutions at even modest solution potential levels.
- It is widely held that this results from the formation of some sort of passivating film on the mineral surface that most likely consists of an altered, partially Fe-depleted sulfide layer.
- Because of this, most investigators have assumed that it is the **anodic** half-cell reaction that limits the overall rate of leaching.
- However, we discovered that it is primarily the **cathodic** half-cell reaction (i.e., ferric reduction) that is slow on the passivated chalcopryrite surface.

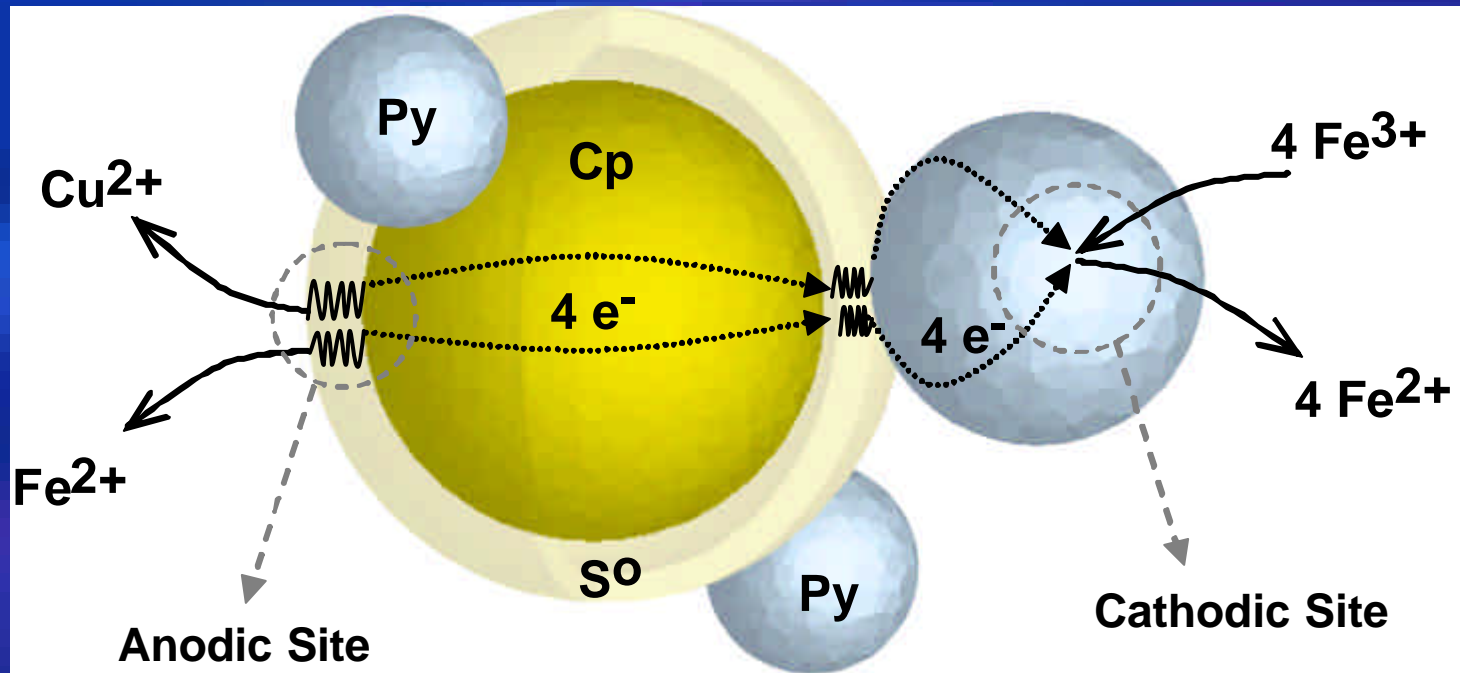


GALVANOX CHEMISTRY

- The presence of pyrite facilitates chalcopryrite leaching by providing an alternative surface for ferric reduction
- This essentially eliminates cathodic passivation of chalcopryrite in ferric sulfate solutions.
- Also, by ensuring rapid chalcopryrite oxidation, the solution potential is easily maintained at levels low enough to prevent anodic passivation of the chalcopryrite
- This also prevents anodic breakdown of the pyrite, which remains more or less completely inert.

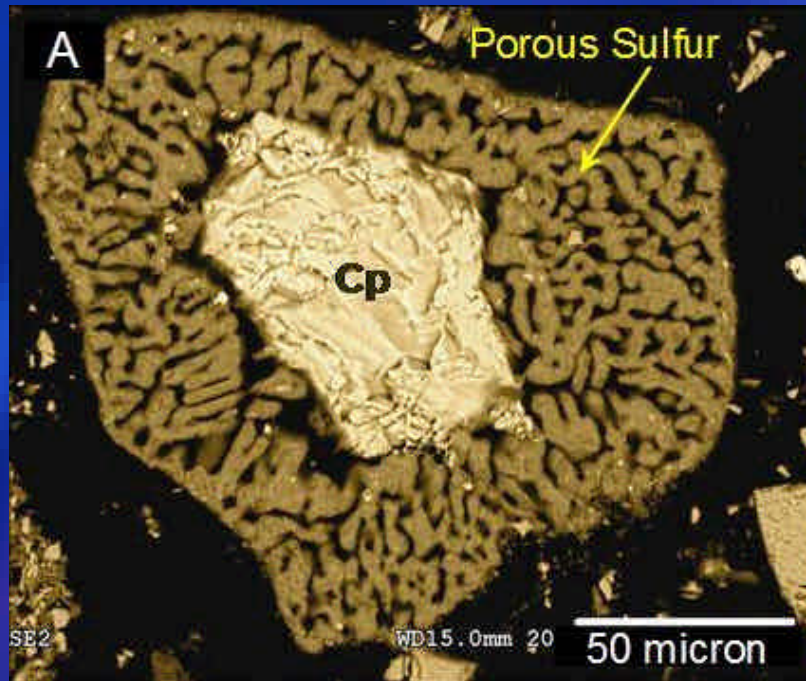


GALVANICALLY-ASSISTED CHALCOPYRITE LEACHING

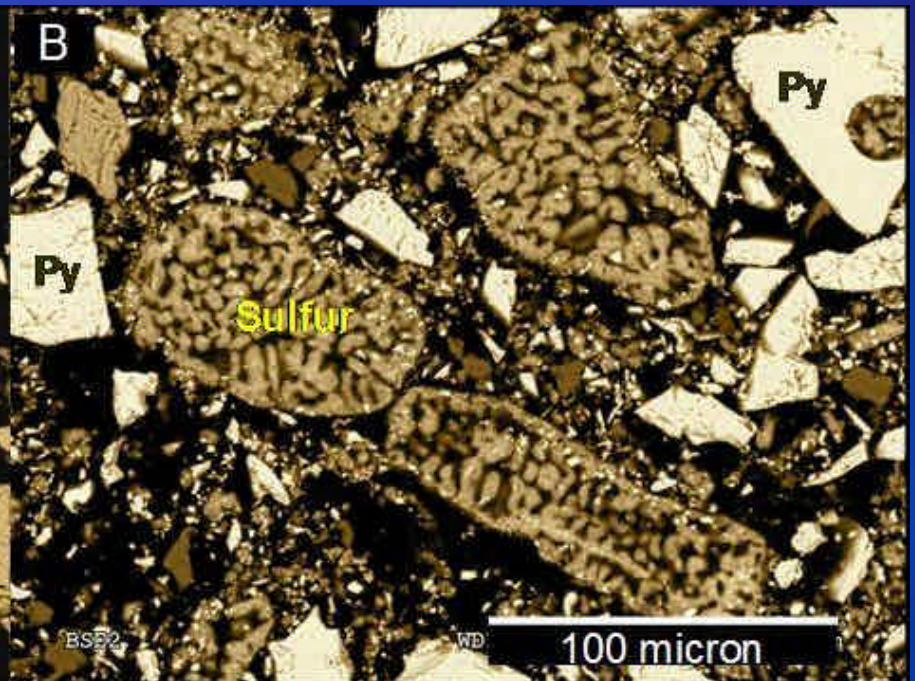




GALVANICALLY-ASSISTED CHALCOPYRITE LEACHING



Partially leached particle

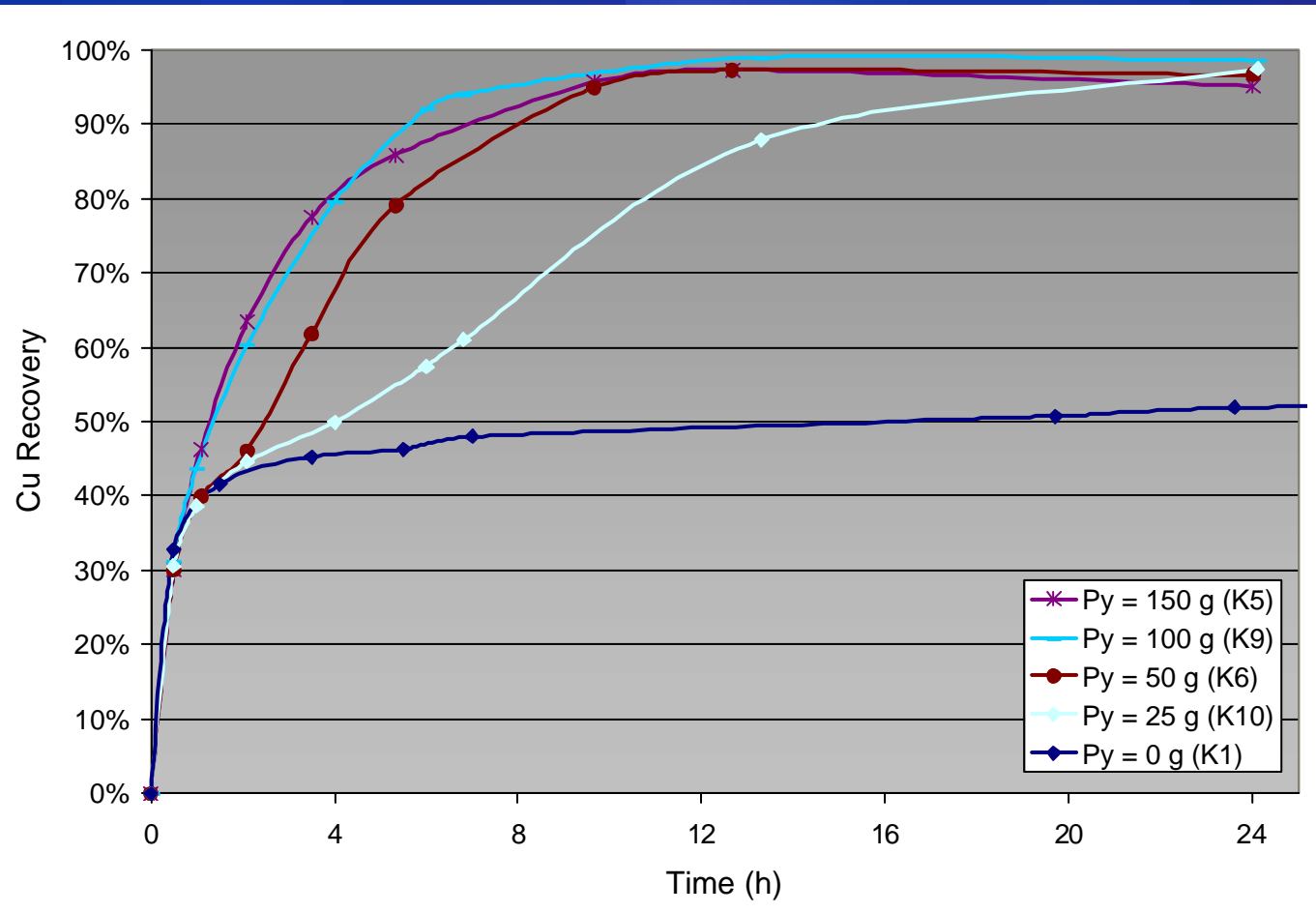


Completely leached particles



CHALCOPYRITE CONCENTRATE – 35% Cu

Effect of pyrite addition (50 g con, 65 g acid, 470 mV, 80°C)





Problem Driven Examples

- Copper Leach SX-EW – key was Cu SX reagent formulation
- Nickel Laterite Leaching – key was HPAL digestion of nickel ores and reprecipitation of iron at high temperature
- Zinc Pressure Leach – break the zinc – acid relationship in the Roast-Leach-Electrowin Process – key was development of the use of surfactants to disperse elemental sulfur during zinc leaching
- Mt. Gordon and Sepon Copper Processes – Chalcocite/pyrite and Clay (Sepon) deposits
- PLATSOL Process – Leach Cu, Ni, Co, Pt, Pd, Au
- Boleo Process – Treat Clay Deposit for Cu, Co, Zn, Mn



Two Process Examples

- The **Boleo Process** is applied to the recovery of copper, cobalt, zinc and manganese from a mixed sulfide/oxide deposit hosted in clay.
- The keys to process development for Boleo were;
 - novel seawater based leaching
 - high rate thickening for solid/liquid separation
 - CSIRO DSX technology for Co-Zn recovery from Mn
 - Mn precipitation as manganese carbonate by-product.
- The **PLATSOL™ Process** is applied to process mixed base and precious metal sulfide concentrates containing copper, nickel, cobalt, platinum, palladium, gold and silver
- The key process development for PLATSOL™
 - chloride assisted total pressure oxidation of bulk sulfide concentrates to extract base and precious metals into an autoclave solution.



**Boleo Project
Adjacent to Santa
Rosalia
Baja California, Mexico**





SANTA ROSALIA LOOKING EAST



Boleo Project

- The Boleo deposit
 - 277 million tonnes @1.77% Cu. Eq grade of measured and indicated
 - 253 million tonnes @ 1.29% Cu Eq. grade of inferred material
- The ore will be treated by a hydrometallurgical process involving acid – seawater leaching with recovery of copper and cobalt metal cathode, zinc sulfate crystal and eventually manganese carbonate precipitate.
- 7,500 tpd of ore to produce
 - 60,000 tpa Cu
 - 2100 tpa Co
 - 36,000 tpa $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$
 - +100,000 tpa MnCO_3



Boleo Project History

- Four substantial departures from early work on Boleo
 - High Rate Thickening for S/L Separation – treat solutions for metal recovery – Clay Ores
 - Copper SX/EW as LME Grade A Cathode
 - Co/Zn Recovery using Solvent Extraction
 - Mn precipitation as MnCO_3
- 2004 Proof of Principle Pilot Plant and 2006 Demonstration Pilot Plant



Boleo Project History

➤ Sulfides

- Cu – very fine chalcocite
- Minor chalcopyrite, bornite and covellite
- Co - cupriferous carrollite and cobaltiferous pyrite
- Zn - sphalerite

➤ Gangue

- Major factor metallurgical process
- Clay dominant (typically 40-50% montmorillonite clay)
- Pulp rheology, settling and filtration
- Carbonates – impact on acid consumption



- Acid Oxidation and Acid Reduction Oxidation leaching (acid leaching with manganese dioxide in the ore)
- Oxidation leaching (addition of acid)
 - $\text{Cu}_2\text{S} + 2\text{MnO}_2 + 4\text{H}_2\text{SO}_4 = 2\text{CuSO}_4 + 2\text{MnSO}_4 + \text{S} + 4\text{H}_2\text{O}$
 - $\text{ZnS} + \text{MnO}_2 + 2\text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{MnSO}_4 + \text{S} + 2\text{H}_2\text{O}$
 - $\text{CoS} + \text{MnO}_2 + 2\text{H}_2\text{SO}_4 = \text{CoSO}_4 + \text{MnSO}_4 + \text{S} + 2\text{H}_2\text{O}$
- Reduction leaching (addition of sulfur dioxide to the ore slurry)
 - $\text{MnO}_2 + \text{SO}_2 = \text{MnSO}_4$



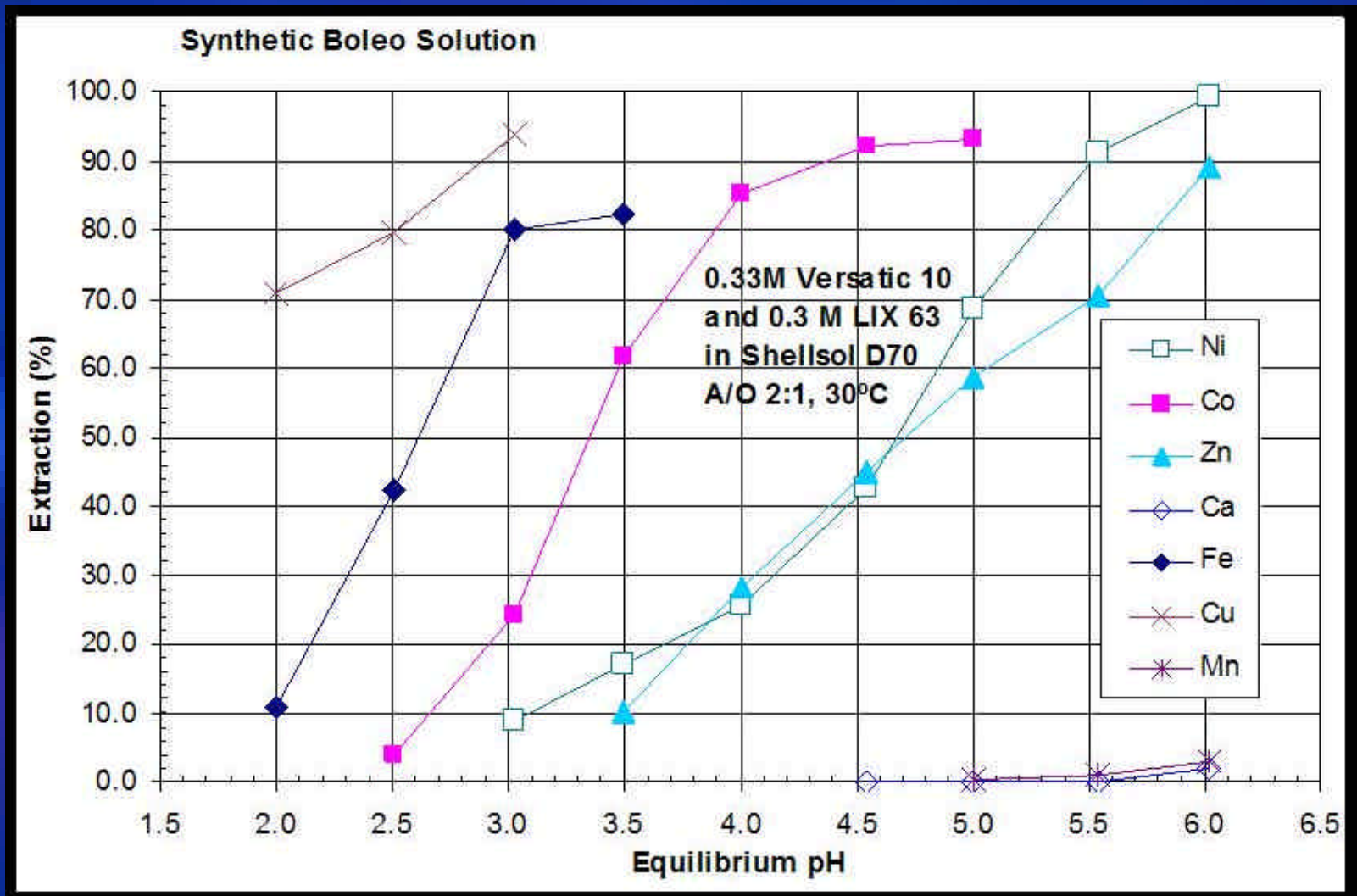
METALLURGICAL TREATMENT OF BOLEO ORE – Partial Neutralization - CCD

- The leach slurry is partially neutralized using local limestone
- Limestone purity is about 60-65%
- High Rate Thickening – 2-3% Solids Using Thickener O/F
- Pocock, Outokumpu and GLV testing

- PLS advances to Cu SX-EW, raffinate is split between return to leach and Co/Zn/Mn recovery



Typical CSIRO DSX Result





ZINC SULFATE AND COBALT METAL RECOVERY FROM DSX STRIP SOLUTION

- Zinc as zinc sulfate and cobalt as metal
- Zinc Extraction
 - $\text{ZnSO}_4 + 2\text{HR}(\text{org}) + \text{Na}_2\text{CO}_3 = \text{ZnR}_2(\text{org}) + \text{Na}_2\text{SO}_4 + \text{CO}_2(\text{g}) + \text{H}_2\text{O}$
- Zinc Stripping
 - $\text{ZnR}_2(\text{org}) + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + 2\text{HR}(\text{org})$
- Zinc Sulfate Recovery
 - $\text{ZnSO}_4 (\text{aqueous}) + x\text{H}_2\text{O} = \text{ZnSO}_4 \cdot x\text{H}_2\text{O} (\text{crystals})$
- Cobalt Extraction
 - $\text{CoSO}_4 + 2\text{HR}(\text{org}) + \text{Na}_2\text{CO}_3 = \text{CoR}_2(\text{org}) + \text{Na}_2\text{SO}_4 + \text{CO}_2(\text{g}) + \text{H}_2\text{O}$
- Cobalt Stripping
 - $\text{CoR}_2(\text{org}) + \text{H}_2\text{SO}_4 = \text{CoSO}_4 + 2\text{HR}(\text{org})$
- Cobalt Electrowinning
 - $\text{CoSO}_4 + \text{H}_2\text{O} = \text{Co} + \text{O}_2(\text{gas}) + \text{H}_2\text{SO}_4$



MANGANESE CARBONATE RECOVERY FROM DSX RAFFINATE

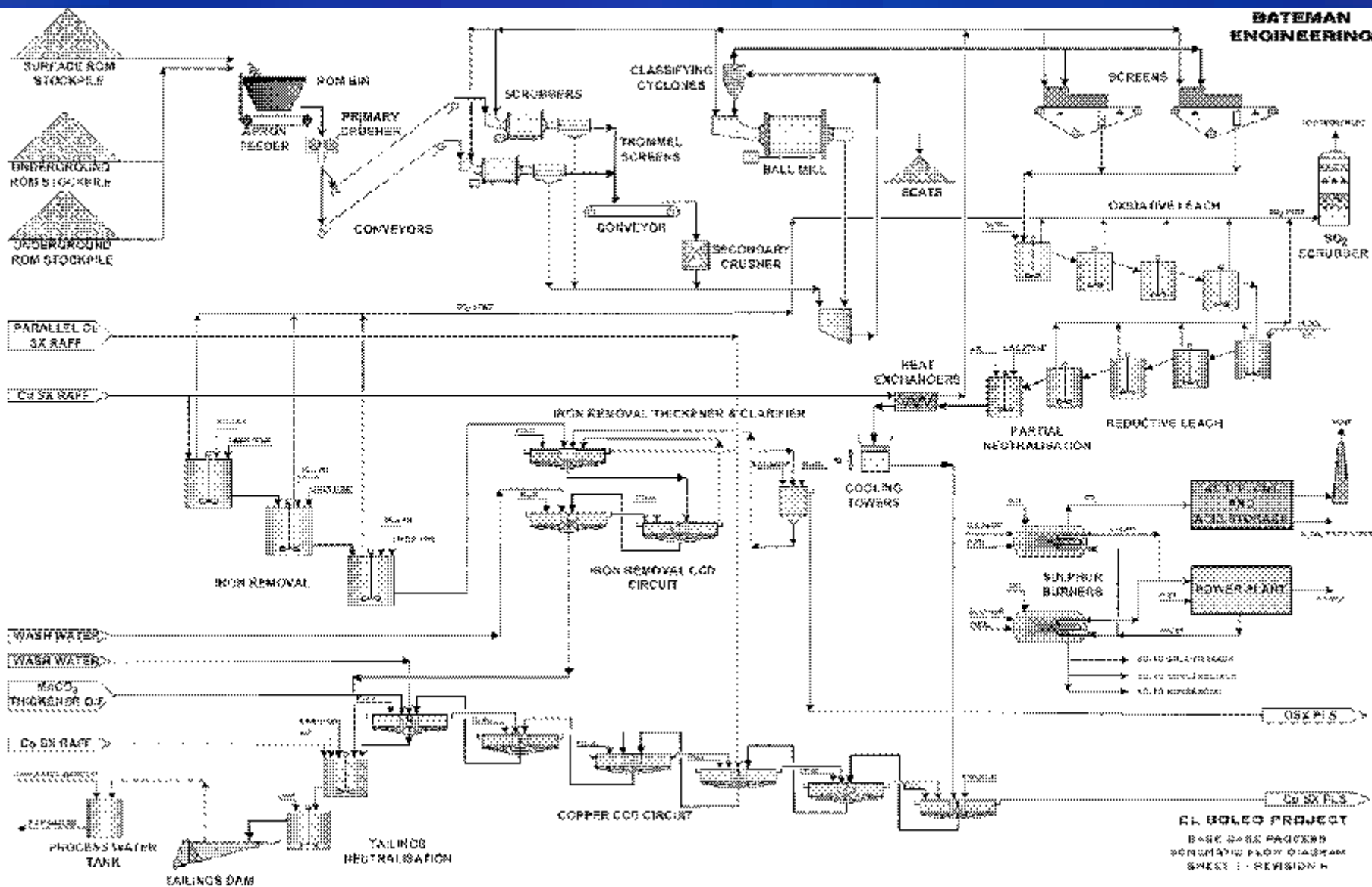
- Manganese Precipitation
- Manganese carbonate can be selectively precipitated using sodium carbonate
 - $\text{MnSO}_4 + \text{Na}_2\text{CO}_3 = \text{MnCO}_3 + \text{Na}_2\text{SO}_4$



- Whole ore leaching of the Boleo Ore
- Leach circuit designed for maximum metal extraction with minimum reagent consumption and cost
- Seawater based
- High rate thickeners for CCD
- Conventional SX/EW for Cu
- Separation of cobalt and zinc using CSIRO DSX Extractant
- Cobalt as metal by SX/EW
- Zinc as zinc sulfate crystal
- Manganese by-product will be manganese carbonate

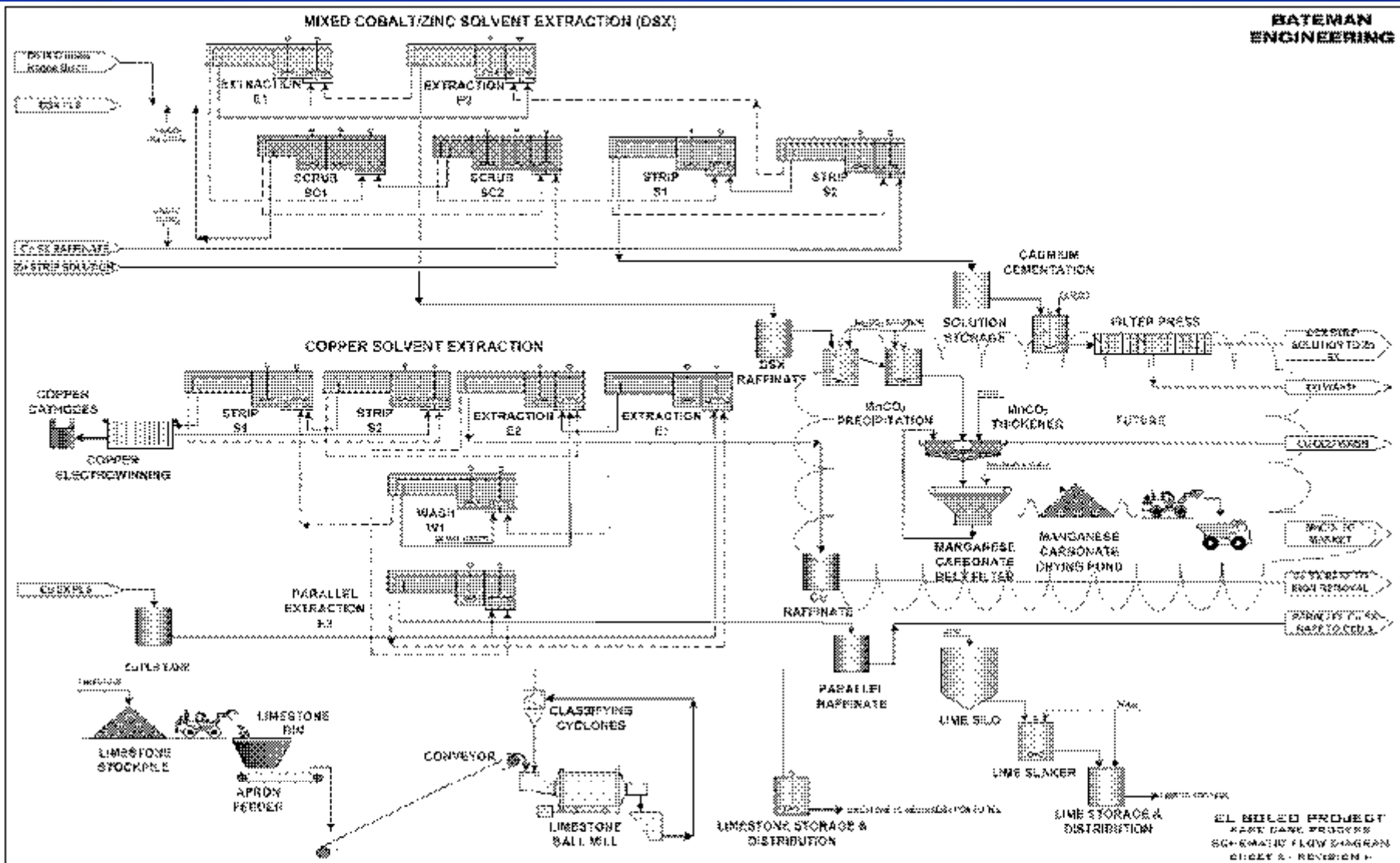


Flowsheet – Part 1



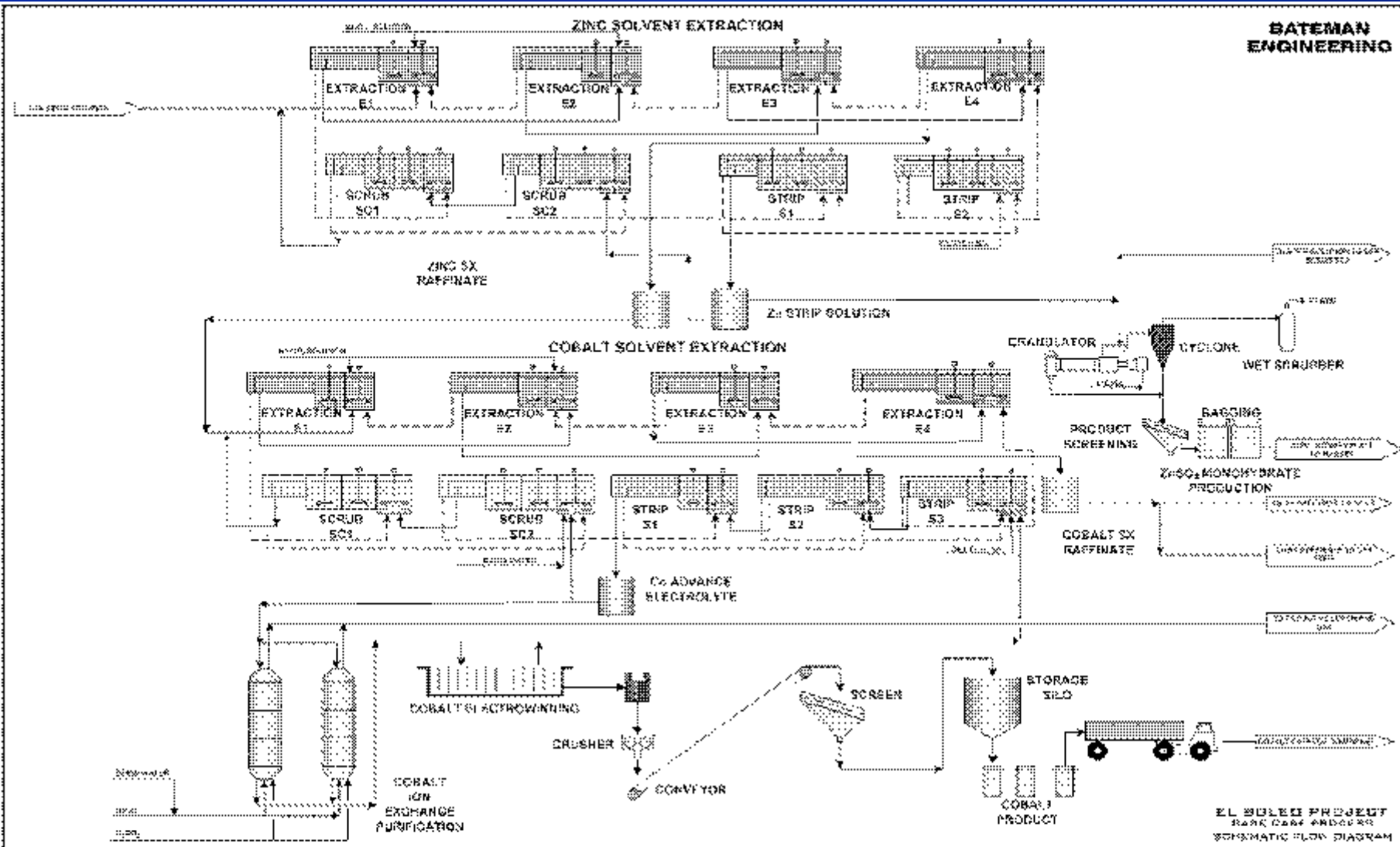


Flowsheet – Part 2





Flowsheet – Part 3





DEMONSTRATION PILOT PLANT RESULTS

- 14 kg/hr for 16 days - 5 tonnes of total material
- Feed samples

Chemical Analysis (%)										
Sample	Cu	Co	Zn	Mn	Fe	Ca	Mg	Al	Ni	Si
1	2.16	0.102	0.48	4.14	8.04	NA	2.75	5.29	0.014	18.7
2	2.25	0.123	0.47	5.58	8.15	NA	2.76	5.21	0.011	19.4
3	2.26	0.141	0.48	5.99	8.22	0.996	2.74	5.39	0.013	18.5
4	2.26	0.124	0.53	4.27	8.9	0.978	3.08	4.93	0.013	20.4
5	2.27	0.157	0.50	5.21	7.9	1.32	2.86	5.35	0.017	19.0
6	2.18	0.137	0.51	5.25	8.59	1.16	2.96	5.67	0.016	20.1
7	2.04	0.155	0.46	5.45	7.71	1.03	2.67	4.73	0.015	20.6
8	2.04	0.137	0.50	4.16	8.58	0.979	3.01	4.83	0.016	21.2
Average	2.18	0.135	0.49	5.01	8.26	1.08	2.85	5.18	0.014	19.7



➤ Leach Extraction

OL2 pH	RL2 ORP	H ₂ SO ₄	SO ₂	Limestone	Extraction (%)			
					Cu	Co	Zn	Mn
1.7	399	225	80	68	90.9	82.6	53.9	97.1
1.5	397	235	73	75	90.9	81.4	55.4	96.4
1.4	399	315	124	113	92.7	83.8	61.0	98.0
1.2	427	513	152	368	94.4	90.3	72.3	96.7

- Extraction based on residue assay after CCD 6
- Design at pH 1.7 for Oxidative Leach



LEACH PILOT PLANT





- CCD Results – 6 stage “High Rate” Thickener Circuit
- Dilution of the feed to ~ 3% solids was effective
- The solids settled rapidly, producing a well clarified, low-solids overflow as feed to copper SX.
- Outokumpu, Pocock Industrial and GL and V – independent testwork using Pilot Plant Samples
- Vendor results used to size and design thickeners



CCD - PILOT PLANT





➤ Copper Metal Assays

Sample	Analysis (g/t)										
	Se	Te	Bi	Sb	Pb	As	Fe	Ni	Sn	Ag	S
Cathode 1	<1	<1	<1	<1	<1	<1	2.4	<1	<1	<25	<15
Cathode 2	<1	<1	<1	<1	1.2	<1	1.4	<1	<1	<25	17.4
Cathode 3	<1	<1	<1	<1	<1	<1	1.3	<1	<1	<25	<15





Co, Zn Recovery by DSX

- CSIRO DSX system
- 13.2% LIX 63 and 6.25% Versatic 10 in Orfom SX80CT
- 3E stages (pH ~ 4.5)
- 2 scrub stages (with zinc sulfate solution)
- 2 zinc strip stages at pH 3.2
- 2 bulk strip stages at pH 1
- +99% Extraction and Recovery of Co/Zn - ~ 0% Extraction of Mn



DSX Results



Zinc Strip Solution



Cobalt Strip Solution

Excellent Recovery and Separation of Zinc and Cobalt away from Manganese
For Final Design Moved to a Single Bulk Strip



Zn SX Results

- 30% Cyanex 272 in Orfom SX 80CT
- 4 E at pH 2.6 – 2.9
- 2 scrub stages (using zinc strip solution)
- 2 strip stages at pH 1.
- Raffinate ~ 100 mg/L Zn.
- Zn strip solution approached 80 g/L (80,000 mg/L Zn) with Zn:Co ratio of 4,000:1
- Subsequent work has shown up to 160 g/L Zn in strip solution

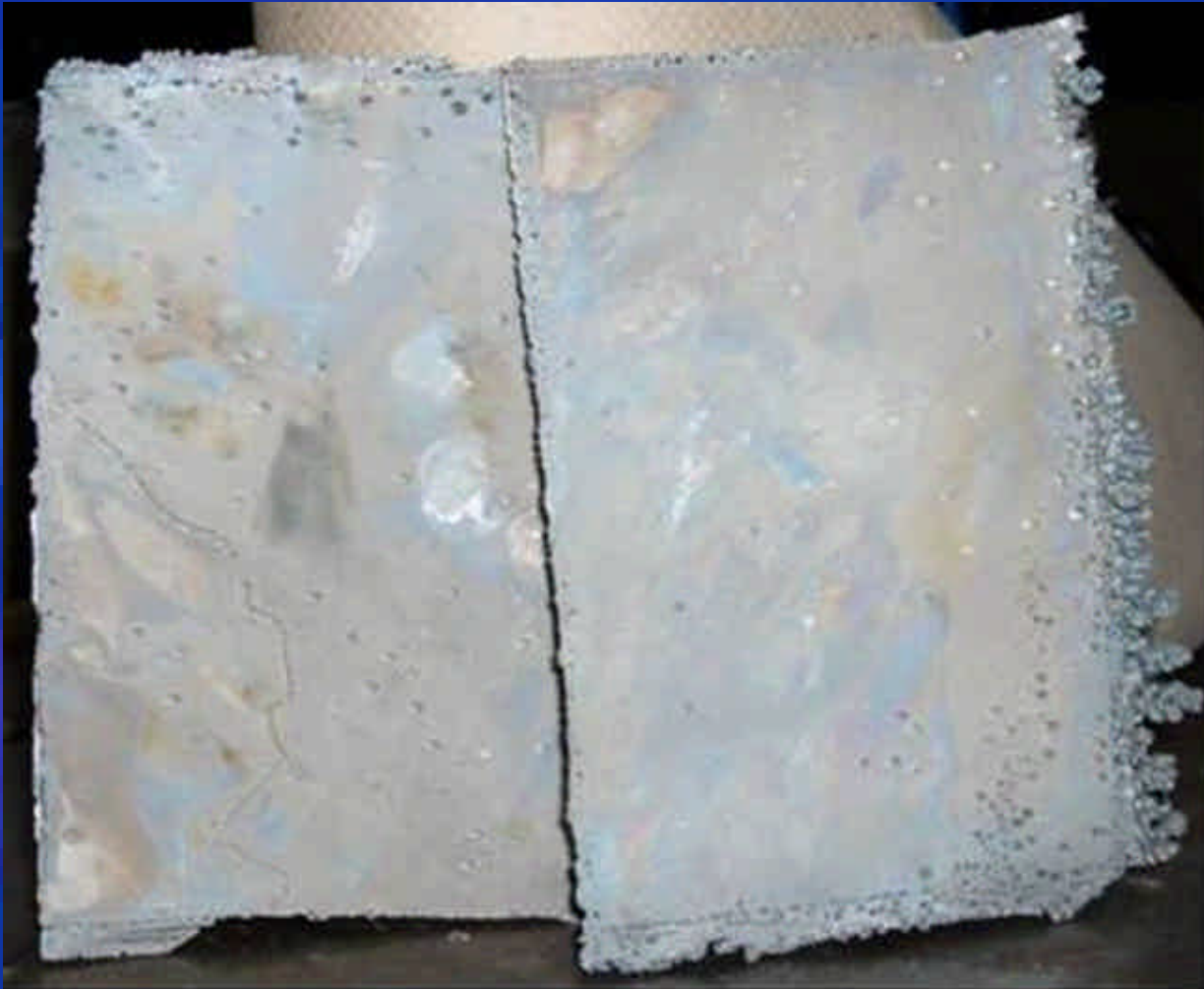


Cobalt SX/EW Results

- 4 E stages at pH 5.2 to 5.5 using 30% Cyanex 272 in Orfom SX 80CT
- 2 stages of scrubbing
- 3 stages of stripping (with spent electrolyte)
- 1 stage of conditioning before organic recycle.
- Co strip solution was polished by using DOWEX M4195 and PUROLITE S-950 resins for minor element capture prior to cobalt electrowinning in a divided cell.
- Cobalt was deposited at 250 A/m² at 70°C.
- Feed of 6000 mg/L of Co with raffinates of less than 1 mg/L
- 90 g/L Co in cell feed



Cobalt Metal





Cobalt Metal Analysis

Sample	Analysis (ppm)						
	Cd	Cu	Fe	Mn	Ni	Pb	Zn
Cathode 1	66	<2	<4	<0.3	55	40	<10
Cathode 2	43	<2	<4	<0.3	56	41	<10



Manganese Carbonate Assay (Typical)

Species	Analysis	Units
Mn	47	%
Ca	1	%
Mg	0.3	%
Na	0.6	%
Al	0.5	%
Ni	350	g/t
Zn	300	g/t
Fe	200	g/t
Cu	<5	g/t
Co	50	g/t
Cd	<5	g/t
CO ₃	45	%
SO ₄	2	%
Cl	100	g/t

200 kg of MnCO₃
Recovered



Next Step – Construction

Example: Sepon Copper and Gold Operation





The PLATSOL™ Process

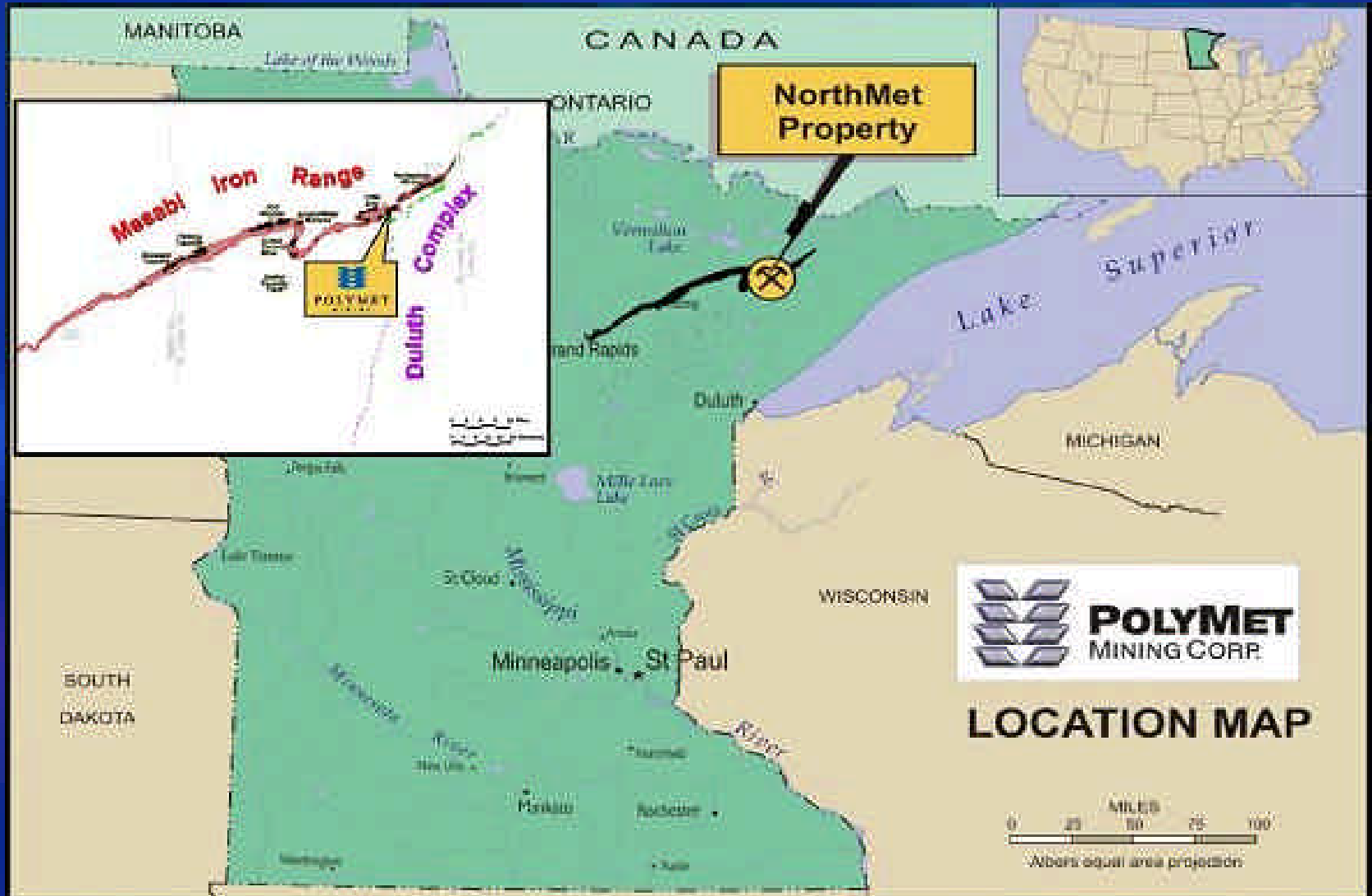


➤ NorthMet (PolyMet Mining)

- Northern Minnesota, adjacent to the historic Iron Range.
- Large, polymetallic sulfide deposit with values in Cu, Ni, Co, Zn, Au and Platinum Group Metals (PGM).
- The NorthMet measured and indicated resource is 638 million tons (August 2007)
- Flotation of Concentrates then PLATSOL™



PolyMet Project - Location





Former LTV Plant Site





Existing Rod and Ball Mills





- Pilot Scale Testwork at SGS Lakefield Research Limited in Ontario, Canada.
 - Mineral Processing
 - Hydrometallurgy
 - Final products copper cathode, Au/PGM Precipitate, Mixed or Separate Ni/Co Hydroxide, Gypsum
- Close to 50 tonnes of material from NorthMet were processed in Pilot Scale Testwork



➤ Two circuits at NorthMet

- Mineral processing flowsheet to produce a bulk concentrate
- Hydrometallurgy flowsheet for recovery of Cu-Ni-Co-Zn-Au-PGM products

➤ Hydrometallurgy

- chloride-assisted leaching of base and precious metals
- metal recovery steps for the base and precious metals



Sample	Weight (t)	Assay (% or g/t)					
		Cu	Ni	S	Pt	Pd	Au
Composite 4	4.4	0.31	0.10	0.91	0.05	0.28	0.08

Produce concentrate containing 10-12% Cu+Ni, 8-12 g/t Pt+Pd+Au



Autoclave Leaching Base Metals

Chloride – Assisted Total Pressure Oxidation (220 C, 6 g/L Cl)

Chalcopyrite Oxidation/Iron Hydrolysis:



Pyrite Oxidation:



Pyrrhotite Oxidation



Nickel Sulfide Oxidation:





Autoclave Leaching Precious Metals

Gold Oxidation/Chlorocomplex Formation:



Platinum Oxidation/Chlorocomplex Formation:



Palladium Oxidation/Chlorocomplex Formation:

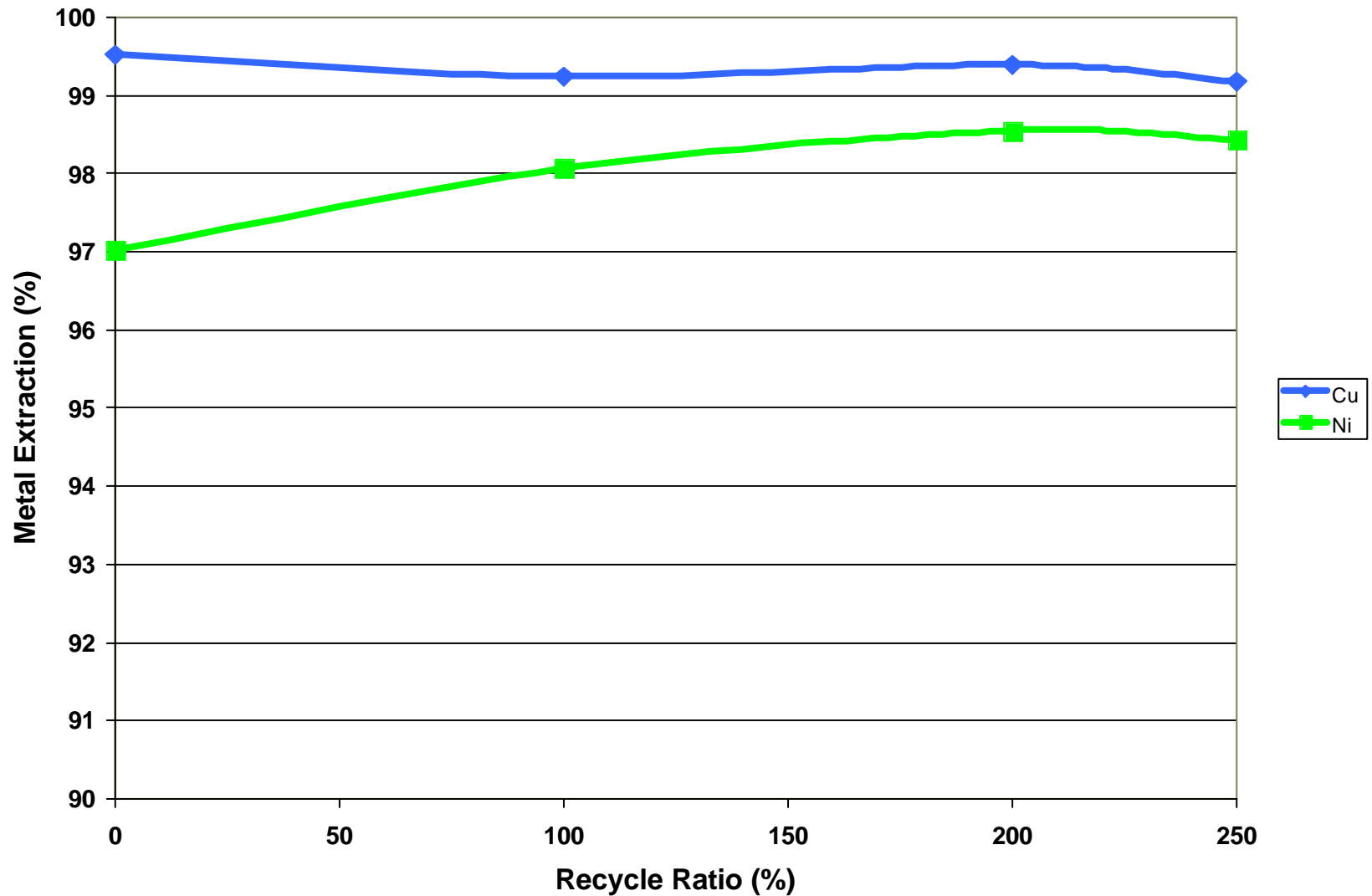


Temperature of 220 to 230°C.

Barren solids washed and discarded

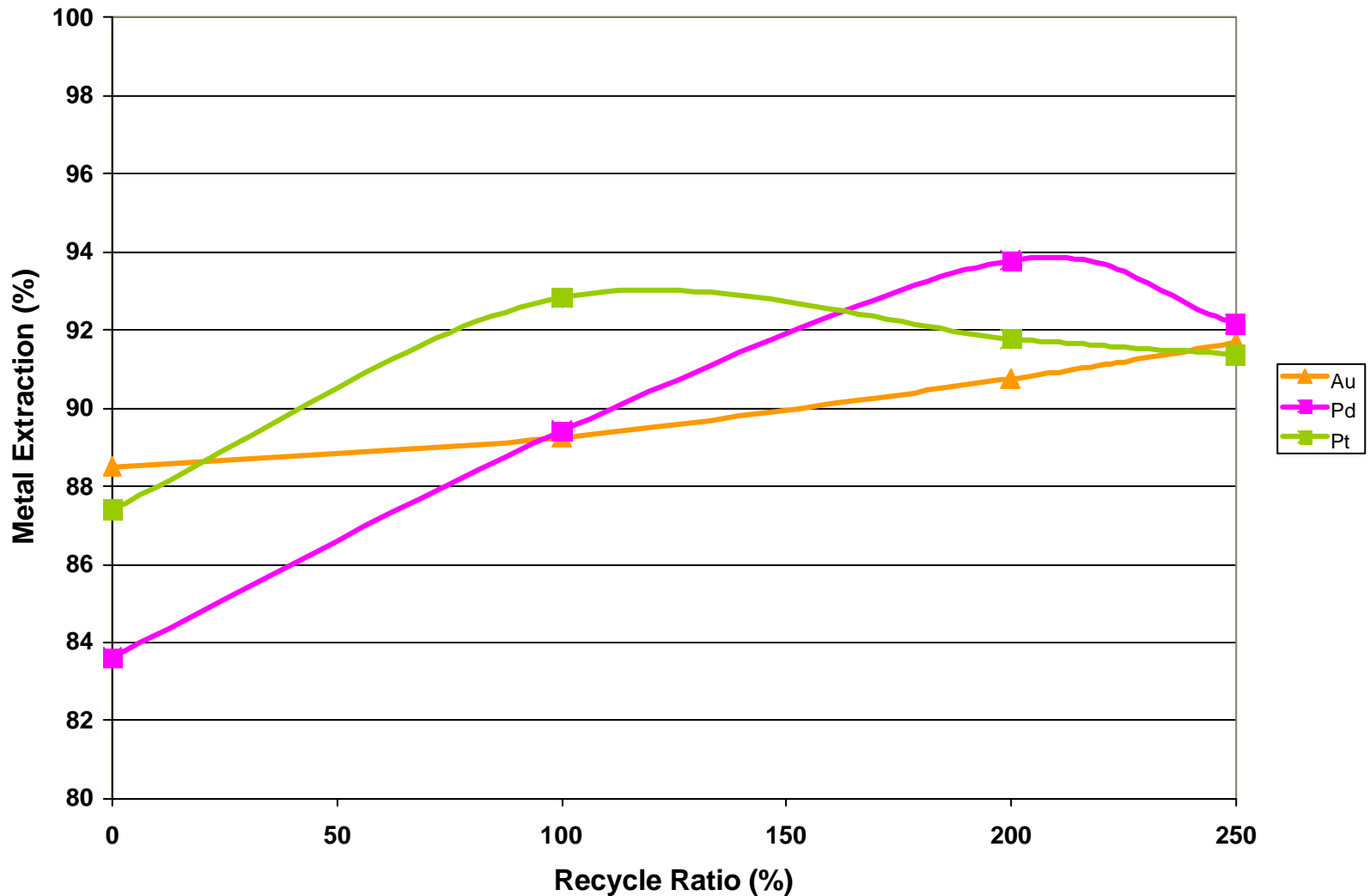


Recycle PLATSOL® Cu and Ni Extraction





Recycle PLATSOL® Au, Pt, Pd Extraction





Au and PGM Precipitation

- Ferric ion must be reduced and then the precious metals precipitated

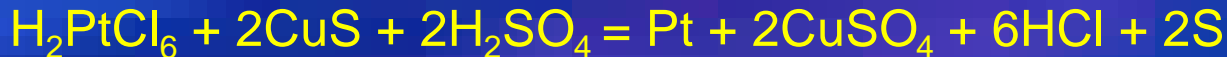
Ferric Reduction



Gold Precipitation



Platinum Precipitation



Palladium Precipitation



- CuS precipitation of gold, platinum and palladium in excess of 99.5%
- Base metal losses were negligible.
- 4 kg of precipitate from 2005 pilot plant
- 56 g/t Au, 211 g/t Pt and 907 g/t Pd. 35.7% Cu and 49% S



Solution Neutralization

- Excess acid from the autoclave is neutralized ahead of Cu SX
- Limestone neutralization with 300% “seed” to grow coarse, clean, crystals of gypsum.
- Gypsum Precipitation
- $\text{H}_2\text{SO}_4 + \text{CaCO}_3 + 2\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- Carbonate utilization exceeded 99% in the pilot tests
- Gypsum Analysis – 98.6% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$



Copper Cathode Assay

	Analysis (g/t)			
Sample	Fe	S	Pb	Ag
Cathode 1	1.02	10.50	0.52	<1
Cathode 2	1.31	6.00	3.63	<1
LME Grade A	10	15	5	25



Raffinate Treatment

- Raffinate is split between return to autoclave for cooling and Ni/Co/Zn recovery
- Raffinate Neutralization
- Fe and Al Removal
 - Two stage oxidation/hydrolysis circuit
 - $\text{Fe} < 5 \text{ mg/L}$, $\text{Al} < 38 \text{ mg/L}$ with negligible Ni/Co loss
- Copper Removal with NaSH Precipitation
 - $\text{CuSO}_4 + \text{NaSH} = \text{CuS} + 0.5\text{Na}_2\text{SO}_4 + 0.5\text{H}_2\text{SO}_4$
- In the 2005 pilot plant, $\text{Cu} < 50 \text{ mg/L}$
- CuS to Au/PGM Recovery



Ni/Co Mixed Hydroxide Route

Two Step Precipitation – First with MgO then CaO

Nickel Precipitation with Magnesia



Cobalt Precipitation with Magnesia



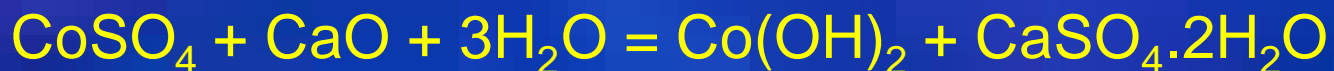
Zinc Precipitation with Magnesia



Residual Nickel Precipitation with Lime



Residual Cobalt Precipitation with Lime



Residual Nickel Precipitation with Lime



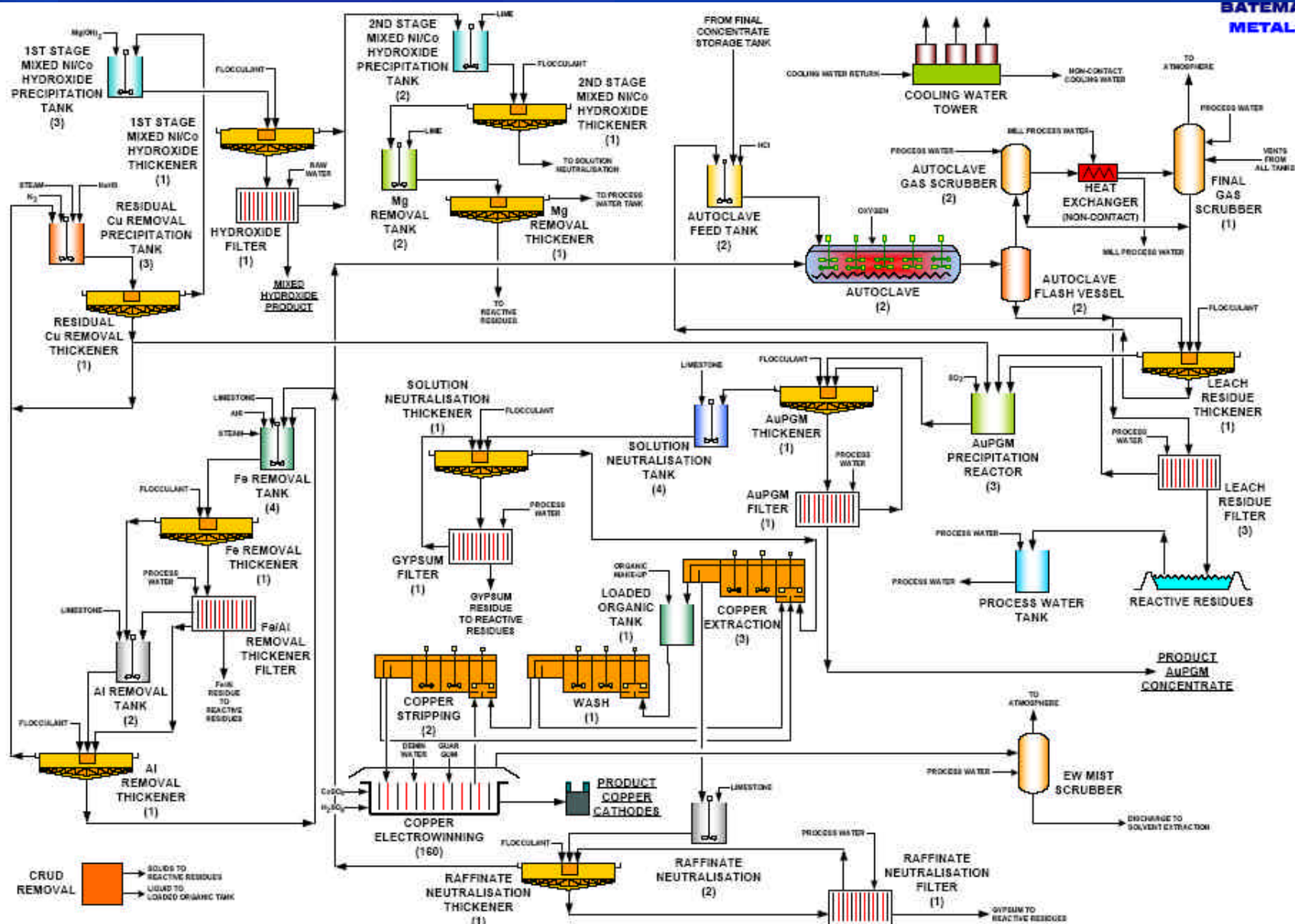


Mixed Hydroxide Product

Sample	H ₂ O	Ni	Co	Cu	Fe	Zn	Al	Mg	Ca	Si	Mn
	%	%	%	%	%	%	%	%	%	%	%
1	51.2	36.3	1.92	0.37	0.59	4.84	0.07	1.04	0.02	0.05	0.03
2	41.2	31.5	1.67	0.31	0.51	4.31	0.04	0.62	0.04	0.03	0.02
		31.3	1.67	0.32	0.54	4.27	0.04	0.62	0.04	0.03	0.02
3	56.3	40.6	2.17	0.41	0.68	0.56	0.05	0.76	<0.08	0.04	0.03



**BATEMAN
METALS**





➤ Continuous Pilot Plant Successfully Completed

- Bulk Concentrate Production Demonstrated
- Hydromet Process for Concentrate Treatment Demonstrated
 - Copper Cathode of LME Grade A Quality
 - Au and PGM Precipitate for Toll Processing
 - Mixed Hydroxide Product Containing Ni-Co-Zn
 - Synthetic Gypsum



Conclusions

- Hydrometallurgical processing of complex ores and concentrates offers the possibility of unlocking new and valuable mineral deposits for production of metals.
- The Boleo process offers the promise of being able to unlock the value in a complex, clayey ore containing significant amounts of copper, cobalt, zinc and manganese.
 - High rate thickeners
 - CSIRO DSX
 - Manganese Carbonate
- The PLATSOL™ process has opened the way to treat the NorthMet ore of PolyMet mining.
 - Small additions of chloride to extract platinum, palladium and gold.



Thank You!

Any Questions?