Keynote address: hydrometallurgical process development for complex ores and concentrates
by D. Dreisinger*

Synopsis
Hydrometallurgical processing of complex ores and concentrates is becoming increasingly important as the mining and metallurgical industry seeks to exploit mineral deposits that are difficult to treat using conventional mineral processing and pyrometallurgical technologies. Mineral processing is often challenged by the difficulty or inability to separate valuable minerals into marketable concentrates. Hydrometallurgical processing, using selective leaching technology, can often ‘chemically beneficiate’ such difficult deposits. Pyrometallurgical treatment of base metal concentrates is capital intensive and subject to ever more stringent environmental control. Hydrometallurgical processing is generally lower in capital cost for an equivalent metal production rate and avoids the gas and dust issues associated with pyrometallurgical processing. The possibility of by-product recovery may also increase with hydrometallurgical treatment. Two examples of new technology or flowsheet development for treatment of complex ores and concentrates are used as illustration. These include the El Boleo process of Baja Mining for recovery of copper, cobalt, zinc and manganese from a complex clayey ore and the PLATSOL™ process for recovery of copper, nickel, cobalt, platinum, palladium and gold from a bulk sulphide concentrate.

Introduction
The treatment of base and precious metal deposits has as a final goal the recovery of final metal products of sufficient purity and in a suitable commercial form to meet customer specifications. Historically for metals like copper, nickel, zinc and lead recovery from sulphide deposits, processing has included mining, flotation of concentrates and finally smelting/refining of the concentrates through to final products (generally high purity metals). However, a number of factors are causing a gradual but steady shift away from the traditional processing routes. Mineral processing technologies may be constrained in the processing of complex ores (fine graded) or ores that contain multiple valuable metals. Hydrometallurgical leaching technology may actually benefit from the fine graded character of the raw material and offers the possibility of recovery of multiple metals from a single feed source. Similarly, pyrometallurgical processing of sulphide concentrates is becoming increasingly expensive, environmental constraints due to emission of gases and production of dusts are increasing and hydrometallurgical processing often results in the losses of valuable metal by-products into slags and residues. Hydrometallurgical technologies have lower capital costs, avoid production of gaseous or dust emissions, and can manage recovery of multiple metals from a single feed source. In this way, hydrometallurgical processing is growing in importance to the global metal industry, as shown in Figure 1.

The success of hydrometallurgy as a technological field lies in the ability to extract valuable metals into solution, purify the metal containing solutions to concentrate valuable metals and reject impurities, and finally to recover a pure metal product by electrolysis, metal precipitation or other means. Advances in hydrometallurgy are rooted in improvements in the science and technology of leaching, solid-liquid separation, solution purification (solvent extraction, ion exchange, cementation) and metal recovery.

The following sections illustrate two new process developments that highlight the potential of hydrometallurgical treatment to solve ‘difficult’ metallurgy and extract base and precious metals into marketable form. The Boleo process is applied to the recovery of copper, cobalt, zinc and manganese from a mixed sulphide/oxide deposit hosted in clay. The keys to process development for Boleo were to incorporate novel seawater based leaching, high rate thickening for solid/liquid separation, the CSIRO DSX

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Mineral Processing        Hydrometallurgy        Pyrometallurgy
Complex ores
Loss of values in tails
TIME
Mineral Processing        Hydrometallurgy        Pyrometallurgy

The PLATSOL™ process was developed to process mixed base and precious metal sulphide concentrates containing copper, nickel, cobalt, platinum, palladium, gold and silver where the grade and nature of the concentrates produced by flotation were not amenable to toll smelting. The PLATSOL™ process uses chloride assisted total pressure oxidation of bulk sulphide concentrates to extract base and precious metals into an autoclave solution. The ability to directly extract precious metals as chloro-complexes is the key to the PLATSOL™ process development.

**The Boleo process**

The Boleo Copper-Cobalt-Zinc-Manganese Project of Baja Mining Corp. is situated adjacent to Santa Rosalia on the Baja Peninsula of Mexico (Figure 2). The Boleo deposit has a large geological resource with 277 million tonnes @ 1.77% Cu Eq grade of measured and indicated and 253 million tonnes @ 1.29% Cu Eq grade of inferred material (www.baja mining.com). The ore will be treated by a hydrometallurgical process involving acid—seawater leaching with recovery of copper and cobalt metal cathode, zinc sulphate crystal and eventually manganese carbonate precipitate.

Process development of the mettallurgical flowsheet for Boleo has gone through bench and integrated pilot-plant testing.

An initial ‘proof of principle’ pilot plant was executed at SGS Lakefield Research in Canada in November 2004. The major focus of the proof of principle pilot plant was to confirm that the clayey Boleo mineralization could be thickened and washed in a conventional CCD train using high rate thickeners and that the CSIRO ‘DSX’ solvent extraction system could be used to recover cobalt and zinc. The DSX system involves mixing LIX 63 with Versatic 10 extractant to improve selectivity for (Co+Zn)/Mn.

Since the initial proof of principle pilot plant in 2004, further work has been undertaken with CSIRO (Australia) to optimize the DSX solvent extractant composition and to add a manganese recovery process to the Boleo flowsheet. The simple addition of sodium carbonate (soda ash) to the DSX raffinate was found to precipitate a manganese carbonate product of high purity. This manganese carbonate material may form a feedstock to the production of manganese chemicals, manganese metal or electrolytic manganese dioxide.

The improved metallurgical flowsheet for Boleo has now been evaluated in a fully integrated demonstration pilot plant at SGS Lakefield Research in Canada.
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Metallurgical treatment of Boleo ore

After a quick review of the major elements of the process, the focus will be on the demonstration pilot plant results. Figures 3–5 show the overall flowsheet in simplified format.

Milling and leaching circuit

The Boleo ores are clayey and generally fine grained and easily broken. The milling circuit design takes material from the ROM pad into a static grizzly with the oversize to a primary crusher. The combined product is then scrubbed in copper solvent extraction raffinate. The scrubber product is screened with the oversize sent to a secondary crusher. The combined product goes to the ball mill sump before cycloning. The coarse cyclone product is directed to the ball mill. Milling is conducted in raffinate. (Figure 3.)

The milled product is heated to a target temperature of 80°C for atmospheric leaching. Leaching proceeds in two steps: acid, oxidative leaching with manganese dioxide oxidation for leaching of Cu, Zn and Co sulphides and: acid reductive leaching with addition of sulphur dioxide gas to reduce residual manganese dioxides. The reductive leaching of surplus manganese dioxide is essential for maximizing the extraction of cobalt.

Oxidation leaching (acid leaching with manganese dioxide in the ore):

\[
\text{Cu}_2\text{S} + 2\text{MnO}_2 + 4\text{H}_2\text{SO}_4 = 2\text{CuSO}_4 + 2\text{MnSO}_4 + 2\text{H}_2\text{O}
\]

\[
\text{ZnS} + \text{MnO}_2 + 2\text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O}
\]

\[
\text{CoS} + \text{MnO}_2 + 2\text{H}_2\text{SO}_4 = \text{CoSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O}
\]

Reduction leaching (addition of sulphur dioxide to the ore slurry):

\[
\text{MnO}_2 + \text{SO}_2 = \text{MnSO}_4
\]

The slurry from oxidation and reduction leaching is then partially neutralized using local limestone that is available on the Boleo mine lease. The purity of the limestone is about 65–70% and it is highly reactive for acid neutralization. A small amount of air is added during partial neutralization to ensure that there is no residual cuprous ion (that may form if reductive leaching goes to too low a redox value) in solution. Cuprous ion is not extracted by conventional oxime solvent extraction reagents.

Solid-liquid separation and CCD washing

The first proof of principle pilot plant confirmed that the Boleo leach pulp could be thickened and washed using high rate thickening. High rate thickening involves the dilution of the incoming slurry (by recycle of overflow from the same thickener) so as to create a dilute slurry (3–5% solids) for flocculation and settling into the thickener bed. This approach was verified by testing performed by Pocock Industrial and by Outokumpu in lab and pilot-scale testing at SGS—Lakefield. The wash solution to be used at Boleo consists of a combination of barren solution (after cobalt, zinc and manganese removal) and fresh brine solution.

Copper solvent extraction and electrowinning

The recovery of copper from complex chloride containing solutions is feasible using modern selective copper solvent extractants combined with a ‘wash stage’ during SX recovery of copper to prevent transfer of chloride from leaching through to electrowinning. This approach has been widely reported at plants in Chile with saline PLS solutions and has been adopted for Boleo as well. High levels of copper extraction are expected due to the low free acid level in solution (after partial neutralization) and the use of a strong oxime formulation. (Figure 4.)

Copper extraction:

\[
\text{CuSO}_4 + 2\text{HR}(\text{org}) = \text{CuR}_2(\text{org}) + \text{H}_2\text{SO}_4
\]

Copper stripping:

\[
\text{CuR}_2(\text{org}) + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + 2\text{HR}(\text{org})
\]

Copper electrowinning:

\[
\text{CuSO}_4 + \text{H}_2\text{O} = \text{Cu} + \text{O}_2(\text{gas}) + \text{H}_2\text{SO}_4
\]

Copper is electrowon conventionally using permanent cathode blank technology. LME Grade A cathode quality was produced in the proof of principle pilot plant and is also expected to be produced in the commercial plant.

The copper solvent extraction raffinate contains free acid (from copper solvent extraction) and so it is advantageous to return a portion of the raffinate to the milling and leaching circuit, to reduce overall use of fresh acid and to concentrate Co, Zn and Mn in solution. The balance of the raffinate is directed to the Co, Zn, Mn recovery circuit.

Iron removal

The removal of iron from the raffinate advancing to Co, Zn, Mn recovery is accomplished with pH adjustment and aeration. The bulk of the iron in solution will be present as ferrous. Ferrous is oxidized and precipitated as ferric hydroxide precipitates. Aluminum will co-precipitate with iron in this step.

Two stages of iron removal were allowed in the pilot-plant design. The first stage is used to precipitate more than 95% of the iron with the second stage precipitation reducing iron to less than 10 ppm residual. The second stage precipitate is returned to oxidative leaching to ensure that any co-precipitated ‘pay-metals’ are recovered. The first stage cake is filtered, washed and then repulped and sent to tailings. The iron removal solution is then advanced to cobalt and zinc solvent extraction.

Cobalt and zinc solvent extraction

CSIRO (Australia) has developed a range of synergistic extractants, tailored to specific metal separations. In the case of Boleo, the major challenge is the extraction of cobalt and zinc without extraction of manganese. The particular synergistic system selected for Boleo is the Versatic 10 – LIX 65 mixture. Cobalt is loaded in preference to zinc, which in turn is loaded in preference to manganese with this system.

The cobalt and zinc circuit is designed for bulk extraction and bulk stripping of zinc and cobalt. Some of the zinc strip solution is also employed as a manganese scrub solution make-up. Zinc and cobalt loading must be done with pH control. The most convenient alkali for this duty is sodium carbonate. Bulk stripping of zinc and cobalt is performed using sulphuric acid and pH control.

Cobalt and zinc solvent extraction (with small amount of Mn co-extraction):

\[
\text{CoSO}_4 + 2\text{HR}(\text{org}) + \text{Na}_2\text{CO}_3 = \text{CoR}_2(\text{org}) + \text{Na}_2\text{SO}_4 + \text{CO}_2(g) + \text{H}_2\text{O}
\]

\[
\text{ZnSO}_4 + 2\text{HR}(\text{org}) + \text{Na}_2\text{CO}_3 = \text{ZnR}_2(\text{org}) + \text{Na}_2\text{SO}_4 + \text{CO}_2(g) + \text{H}_2\text{O}
\]
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Figure 4—Flowsheet for Boleo process – Part 2: cobalt and zinc SX using DSX, zinc sulphate evaporation, manganese carbonate precipitation and limestone milling
Figure 5—Flowsheet for Boleo process – Part 3: zinc and cobalt solvent extraction and cobalt electrowinning

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\[
\begin{align*}
\text{MnSO}_4 + 2\text{HR}(\text{org}) + \text{Na}_2\text{CO}_3 & = \text{MnR}_2(\text{org}) + \text{Na}_2\text{SO}_4 + \text{CO}_2(g) + \text{H}_2\text{O} \\
\text{Manganese scrubbing:} & \\
\text{MnR}_2(\text{org}) + \text{ZnSO}_4 & = \text{ZnR}_2(\text{org}) + \text{MnSO}_4 \\
\text{Zinc and cobalt stripping:} & \\
\text{ZnR}_2(\text{org}) + \text{H}_2\text{SO}_4 & = \text{ZnSO}_4 + 2\text{HR}(\text{org}) \\
\text{CoR}_2(\text{org}) + \text{H}_2\text{SO}_4 & = \text{CoSO}_4 + 2\text{HR}(\text{org}) \\
\text{The fully stripped organic is then recycled back to loading. The DSX raffinate advances to manganese recovery.} & \\
\end{align*}
\]

**Cadmium control**

Cadmium is a minor impurity in the Boleo ore and must be removed from both the zinc/cobalt strip solution prior to zinc sulphate extraction and crystallization and cobalt solvent extraction and electrowinning. The method chosen for cadmium control is zinc dust cementation. Zinc dust is widely used for cadmium control in conventional roast-leach-electrowin (RLE) plants for zinc recovery from concentrates.

In this application, it is important to cement only cadmium and not cobalt. This can be accomplished using a lower temperature and not ‘activating’ the cementation.

**Activation with Cu/As or Cu/Sb is the method used in the removal of cobalt by cementation in conventional RLE plants.**

**Cadmium cementation:**

\[
\text{CdSO}_4 + \text{Zn} = \text{Cd} + \text{ZnSO}_4
\]

**Cobalt metal electrowinning**

The zinc/cobalt (bulk) strip solution from DSX will be treated sequentially by zinc solvent extraction and stripping and then cobalt solvent extraction, stripping and electrowinning. The zinc and cobalt solvent extraction circuits will both use Cyanex 272 extractant. The zinc sulphate strip solution will be sent to zinc sulphate crystallization. The cobalt strip solution is purified and electrowon.

There is provision in the cobalt electrolysis circuit for ion exchange polishing of minor elements prior to sulphate electrowin. The cobalt cathode deposit is harvested, crushed and marketed.

**Zinc extraction (Cyanex 272):**

\[
\begin{align*}
\text{ZnSO}_4 + 2\text{HR}(\text{org}) + \text{Na}_2\text{CO}_3 & = \text{ZnR}_2(\text{org}) + \text{Na}_2\text{SO}_4 + \text{CO}_2(g) + \text{H}_2\text{O} \\
\text{Zinc stripping:} & \\
\text{ZnR}_2(\text{org}) + \text{H}_2\text{SO}_4 & = \text{ZnSO}_4 + 2\text{HR}(\text{org}) \\
\text{Cobalt extraction (Cyanex 272):} & \\
\text{CoSO}_4 + 2\text{HR}(\text{org}) + \text{Na}_2\text{CO}_3 & = \text{CoR}_2(\text{org}) + \text{Na}_2\text{SO}_4 + \text{CO}_2(g) + \text{H}_2\text{O} \\
\text{Cobalt stripping:} & \\
\text{CoR}_2(\text{org}) + \text{H}_2\text{SO}_4 & = \text{CoSO}_4 + 2\text{HR}(\text{org}) \\
\text{Cobalt electrowinning:} & \\
\text{CoSO}_4 + \text{H}_2\text{O} & = \text{Co} + \text{O}_2(\text{gas}) + \text{H}_2\text{SO}_4
\end{align*}
\]

**Zinc sulphate crystallization**

The recovery of zinc as a metal product by electrowinning is technically challenging and probably not cost-effective at a low production rate (notwithstanding the current prices of zinc metal). Hence, the zinc product selected for the Boleo process is zinc sulphate crystals. Zinc sulphate is used in a variety of agricultural formulations (fertilizers and feeds).

**Zinc sulphate crystallization:**

\[
\begin{align*}
\text{ZnSO}_4(\text{aqueous}) + \text{H}_2\text{O} & = \text{ZnSO}_4.\text{H}_2\text{O} (\text{crystals}) \\
\end{align*}
\]

**Manganese carbonate recovery**

The raffinate from the DSX circuit has been subjected to iron/aluminum removal and the use of DSX to recover cobalt and zinc. The DSX is also effective at removing other heavy metals from solution. The remaining cations in solution are largely manganese, magnesium, calcium and sodium. The manganese rich nature of the Boleo ore provides a perfect opportunity for recovery of a manganese by-product from this solution.

The simplest and most cost-effective method to precipitate manganese from solution involves addition of sub-stoichiometric amounts of sodium carbonate to the DSX raffinate. The reason for sub-stoichiometric addition is to prevent co-precipitation of impurities such as calcium and magnesium and various minor elements.

**Manganese precipitation:**

\[
\begin{align*}
\text{MnSO}_4 + \text{Na}_2\text{CO}_3 & = \text{MnCO}_3 + \text{Na}_2\text{SO}_4 \\
\end{align*}
\]

Manganese carbonate is not hydrated and hence is lower in weight (relative to hydroxide precipitates) for shipping off site. Initial proof-of-principle testing indicated that the precipitate graded 46–48% Mn after washing and drying of free moisture.

**Demonstration pilot-plant results**

**Feed preparation**

The blended feed material was sampled during each milling campaign. The average assay was 2.18% Cu, 0.135% Co, 0.49% Zn, 5.01% Mn, 8.26% Fe, 1.08% Ca, 2.85% Mg, 5.18% Al, 0.014% Ni and 19.7% Si. The average particle size for the milled feed was 80% passing 38 microns. The feed rate to leaching was set at 14 kg/h. Over the 16 day pilot plant, approximately 5 tonnes of Boleo feed material were processed.

**Leaching, partial neutralization and countercurrent decantation**

The leaching conditions were varied during the 16-day pilot run. Specifically the pH in oxidative leaching was varied from around 1.2 to 1.7. The extractions of Cu, Co, Zn were generally increased when the pH was lowered. However, the addition of acid to maintain a low pH leach environment can be excessive. The partial neutralization was performed with Boleo limestone addition. This worked well and produced a pH 2 product slurry to CCD. The CCD itself generally performed very well. The use of high rate thickeners with overflow recycle for dilution of the feed to ~3% solids worked well. The solids settled rapidly, producing a well clarified, low-solids overflow as feed to copper SX. (Table I.)

**Copper solvent extraction and electrowinning**

The CCD overflow solution advanced to a conventional solvent extraction and electrowinning circuit utilizing 2E – 1S – 2S configuration. An organic solution of 20% LIX 664N (Cognis) in ORFOM SX80 CT (Chevron Phillips) was used for copper recovery. Copper was electrolyzed on stainless steel blanks at ~ 250 A/m² current density.
The copper concentration in the feed to copper SX was typically between 2 000 and 3 000 mg/l (2–3 g/l) with raffinates ranging between 10 and 50 mg/l. This represents 95–99% copper extraction through most of the pilot-plant run. The raffinate was largely recycled to leach during the pilot plant allowing for secondary recovery of a significant portion of the copper remaining in the first raffinate.

A total of 47.4 kg of copper was plated in 4 cycles during the pilot plant at a current efficiency of 97%. Table II shows the assays for three cathode samples from the pilot plant. With the exception of Cathode 2 with a slightly high level of sulphur in cathode, the copper quality was excellent. It is expected that copper produced commercially at Boleo would exceed requirements for LME Grade A or COMEX Grade 1 cathode. The cathode product was smooth, except for slight nodulation at the edges.

Iron and aluminum removal

The iron and aluminum removal circuit operated successfully, typically producing less than 10 mg/l of residual iron in the feed to the DSX circuit. The circuit was started as a two-stage circuit but after commissioning was changed to one-stage as the second stage circuit was deemed to be superfluous. For the purpose of the pilot plant, supplemental oxidation with hydrogen peroxide addition was required to ensure complete iron oxidation and removal. The iron precipitate thickened well but demonstrated variable filterability, depending on the operating temperature of the circuit (T > 45°C produced a more easily filtered product).

Cobalt and zinc recovery using the DSX circuit

Cobalt and zinc were recovered using the CSIRO DSX system. The extractant used was 13.2% LIX 63 and 6.25% Versatic 10 in Orfom SX80CT. The DSX circuit consisted of 3 extract stages (pH ~ 4.5), 2 scrub stages (with zinc sulphate solution), 2 zinc strip stages at pH 3.2 and 2 bulk strip stages at pH 1. The results were excellent with > 99% recovery of both cobalt and zinc with near perfect rejection of manganese. Selective stripping was trialed—i.e. too much cobalt was stripped in the zinc selective strip. A single bulk strip to zinc and cobalt recovery circuits has been selected for the commercial plant.

Zinc solvent extraction

The zinc solvent extraction circuit used 30% Cyanex 272 in Orfom SX 80CT. The circuit consisted of 4 extraction stages at pH 2.6–2.9, 2 scrub stages (using zinc strip solution) and 2 strip stages at pH 1. The zinc concentration in the raffinate was controlled to around 100 mg/l. The zinc strip solution was gradually increased to nearly 80 g/l (80 000 mg/l Zn). The cobalt concentration of the zinc strip solution was less than 20 mg/l Co (Zn:Co ratio of 4 000:1), confirming an excellent separation of zinc and cobalt.

Cobalt solvent extraction and electrowinning

The raffinate from zinc solvent extraction was processed via cobalt solvent extraction and electrowinning. Cobalt was extracted in 4 stages at pH 5.2 to 5.5 using 30% Cyanex 272 in Orfom SX 80CT followed by 2 stages of scrubbing, 3 stages of stripping (with spent electrolyte) and 1 stage of conditioning before organic recycle. The cobalt 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.

The residual zinc entering the cobalt circuit is extracted and stripped in the conditioning step. The conditioning solution is recycled back to zinc solvent extraction, permitting recovery of this zinc.

The average feed solution concentration was about 6 000 mg/l of Co with raffinates of less than 1 mg/l indicating nearly 100% cobalt recovery in this process. The cobalt strip solutions rose to nearly 90 g/l (again due to optimization) allowing effective cobalt electrolisis.

Table I

<table>
<thead>
<tr>
<th>Oxid Leach pH</th>
<th>Red. Leach ORP (mV vs. Ag/AgCl)</th>
<th>H₂SO₄ (kg/t)</th>
<th>SO₂ (kg/t)</th>
<th>Limestone (kg/t)</th>
<th>Cu (%)</th>
<th>Co (%)</th>
<th>Zn (%)</th>
<th>Mn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7</td>
<td>399</td>
<td>225</td>
<td>80</td>
<td>68</td>
<td>90.9</td>
<td>82.6</td>
<td>53.9</td>
<td>97.1</td>
</tr>
<tr>
<td>1.5</td>
<td>397</td>
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<td>75</td>
<td>90.9</td>
<td>81.4</td>
<td>55.4</td>
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<tr>
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<td>61.0</td>
<td>98.0</td>
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<td>1.2</td>
<td>427</td>
<td>513</td>
<td>152</td>
<td>368</td>
<td>94.4</td>
<td>90.3</td>
<td>72.3</td>
<td>96.7</td>
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</table>

Table II

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analysis (g/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Se</td>
</tr>
<tr>
<td>Cathode 1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Cathode 2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Cathode 3</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

The copper concentration in the feed to copper SX was typically between 2 000 and 3 000 mg/l (2–3 g/l) with raffinates ranging between 10 and 50 mg/l. This represents 95–99% copper extraction through most of the pilot-plant run. The raffinate was largely recycled to leach during the pilot plant allowing for secondary recovery of a significant portion of the copper remaining in the first raffinate.

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Table III shows the analysis of two cobalt samples from the production. The cobalt is of very high purity with respect to key elements. There may be opportunity to further reduce the lead levels in cathode by strontium carbonate treatment of Co EW cell feed. Similarly, even lower levels of Cd in cathode may be achieved by more efficient Cd cementation ahead of the zinc and cobalt solvent extraction circuits.

Manganese carbonate precipitation

The DSX raffinate was treated with sodium carbonate solution to selectively precipitate manganese carbonate as a potential by-product from the Boleo process. The manganese carbonate formed as a fine pinkish precipitate that settled, filtered and washed very well. The typical composition of the manganese carbonate is shown below. Nearly 200 kg of wet MnCO₃ was recovered. (Table IV.)

The Boleo project of Baja Mining Corp continues to move forward to production. The process selected for Boleo involves oxidative and reductive leaching of the milled ore, conventional countercurrent decantation (CCD) washing of the leached ore in high rate thickeners, copper solvent extraction and electrowinning, cobalt and zinc solvent extraction and recovery as zinc sulphate crystals and cobalt metal and finally manganese carbonate production as a by-product.

The demonstration pilot plant for the Boleo project was built and operated at SGS Lakefield Research in Canada in June and July of 2006. A total of about 5 tonnes of blended feed were processed. The optimized extraction of metals yielded 91% Cu, 82% Co, 55% Zn and 97% Mn extraction. These values represent the overall extraction after oxidation and reduction leaching, partial neutralization and CCD 6 washing. The oxidation leach condition was set at pH 1.5 to 1.7 to control the addition of acid. The leach residue was effectively settled and washed in a 6-stage countercurrent decantation circuit using ‘high–rate’ thickener design. Copper was very efficiently recovered by SX/EW and electrowon as smooth, high purity copper cathode. A portion of the copper raffinate was treated to remove iron and aluminum by oxidation and pH adjustment followed by DSX recovery of cobalt and zinc. The CSIRO DSX system performed extremely well with >99% recovery of cobalt and zinc from the DSX feed with nearly complete manganese rejection. Zinc was recovered as high purity zinc sulphate solution and cobalt was recovered as cathode metal of high purity. Finally, manganese carbonate grading up to 47% Mn was recovered by precipitation with sodium carbonate.

The PLATSOL™ process

PolyMet Mining Corp. (PolyMet) is advancing the development of the NorthMet Project. The NorthMet deposit is located in northern Minnesota, adjacent to the historic Iron Range. The deposit was discovered in the 1960s and consists of a large, magmatic, disseminated sulphide, polymetallic deposit with values in Cu, Ni, Co, Zn, Au, Ag and platinum group metals (PGM). The shallow, tabular orebody may be mined by open-pit methods with minimal pre-strip and a low waste:ore strip ratio.

The NorthMet deposit is large with measured and indicated resources of 638.2 million tonnes and an inferred mineral resource of a further 251.6 million tonnes. Within this resource, there is a proven and probably reserve of 274.7 million tonnes and the operating plan is to mine 224 million tonnes of this reserve over the 20-year life of the operation (32 000 tpd).

A definitive feasibility study (DFS) has been completed by Bateman Engineering (Australia) in 2006. The project is currently in the environmental permitting phase of the project.

The heart of the processing strategy revolves around the acquisition of the Erie Plant from Cleveland Cliffs. The Erie plant acquisition allows for PolyMet to proceed with a ‘brownfields’ processing strategy with an existing 100 000 tpd crushing and grinding plant and associated infrastructure (roads, power, railway, water supply) including waste disposal. The Erie plant was built in the 1950s for approximately $355 million USD and operated until 2001 processing taconite ore. The acquisition of this plant and related

### Table III

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cd (ppm)</th>
<th>Cu (ppm)</th>
<th>Fe (ppm)</th>
<th>Mn (ppm)</th>
<th>Ni (ppm)</th>
<th>Pb (ppm)</th>
<th>Zn (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode 1</td>
<td>66</td>
<td>&lt;2</td>
<td>&lt;4</td>
<td>&lt;0.3</td>
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### Table IV

<table>
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<th>Species</th>
<th>Mn (%)</th>
<th>Ca (%)</th>
<th>Mg (%)</th>
<th>Na (%)</th>
<th>Al (%)</th>
<th>CO₃ (%)</th>
<th>SO₄ (%)</th>
<th>Ni (%)</th>
<th>Zn (%)</th>
<th>Fe (%)</th>
<th>Cu (%)</th>
<th>Co (%)</th>
<th>Cd (%)</th>
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<td>100</td>
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infrastructure has provided most of the heavy equipment needed for production. Initial plans are to use approximately one-third of the existing plant capacity.

Figure 6 shows the NorthMet site in northern Minnesota, adjacent to the Mesabi Iron Range. Figure 7 provides an overview of the Erie plant site with the tailings area in the background. Figure 8 shows the (existing) indoor view of the Erie plant milling circuit with parallel rod and ball mill lines.

The current development strategy for NorthMet is to produce a saleable concentrate product upon plant start-up and then move to implementation of a hydrometallurgical process plant for recovery of the valuable metals. The PLATSOL™ process has been selected.

The DFS programme has included several pilot-scale test programmes at SGS Lakefield Research Limited in Ontario, Canada. Pilot-plant tests have been performed on ore flotation to produce bulk concentrate samples and on hydrometallurgical treatment of the bulk concentrate materials. The ‘base case’ flowsheet involves high temperature chloride-assisted leaching (PLATSOL™), solid-liquid separation and washing, PGM/Au precipitation, neutralization and Cu SX/EW to produce copper cathode. A portion of the Cu SX raffinate is treated for nickel and cobalt recovery (the remainder is recycled to the autoclave) sequentially by neutralization, first and second stage iron/aluminum removal, residual copper removal by precipitation as a sulphide, first stage Ni/Co/Zn precipitation with magnesia, second stage Ni/Co/Zn precipitation with lime, and then magnesium removal with lime. The product from this treatment is a ‘mixed’ hydroxide of nickel, cobalt and zinc.

NorthMet process flowsheet and pilot-plant studies

The overall NorthMet process flowsheet involves two distinct circuits: a classical mineral processing flowsheet to produce a bulk concentrate and a hydrometallurgy flowsheet for extracting Cu-Ni-Co-Zn-Au-PGM from the bulk concentrate. The further separation of the bulk concentrate into copper and nickel concentrates for sale is a further refinement of the
Figure 8—The Erie plant milling circuit with parallel rod and ball mill lines

Table V

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (t)</th>
<th>Assay (% or g/t)</th>
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<td></td>
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<td>Composite 2</td>
<td>19.2</td>
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<tr>
<td>Composite 3</td>
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<tr>
<td>Start-up material</td>
<td>3.6</td>
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<tr>
<td>Composite 4</td>
<td>4.4</td>
<td>0.31</td>
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</table>

*Composites 1–3 were processed in 2005 and the start-up material and composite 4 were processed in 2006.

basic flowsheet. The hydrometallurgy flowsheet involves chloride-assisted leaching of base and precious metals followed by a series of metal recovery steps for the base and precious metals.

Figures 9, 10 show the process flowsheets in pictorial form. Figure 9 is the mineral processing flowsheet (to produce a bulk concentrate) with Figure 10 showing the hydrometallurgy circuit. The pilot-scale tests for the DFS at SGS-Lakefield were performed in 2005 and 2006. The ore samples sent to SGS-Lakefield comprised four composites and a sample of assay reject material that was used as ‘start-up’ material for the flotation pilot plant. The ore samples were processed through crushing, grinding and flotation to produce a series of bulk concentrates for hydrometallurgical pilot-plant testing. Table V summarizes the pilot plant feed assays and weights processed.

The following is a general description of each part of the proposed plant along with selected results from the 2005 and 2006 continuous pilot testing of the process at SGS Lakefield. The pilot-scale tests at SGS Lakefield form the test work basis for the final feasibility study design for the NorthMet plant.

Crushing, grinding and flotation

The crushing, grinding and flotation circuit (Figure 9) receives ore from the mine into a coarse crusher dump pocket. The ore then proceeds through primary, secondary, tertiary and quaternary crushing followed by rod and ball milling to a size of 100–125 \( \mu m \) \( P_{80} \). The crushing and grinding circuits are existing circuits within the ‘Cliff’s Erie’ plant and will utilize only a third of the available capacity.

The flotation circuit is designed to produce a bulk concentrate carrying pay metals and a tailing with low residual sulphur content. The float circuit has the following elements:

- Rougher conditioning with potassium amyl xanthate (PAX)
- Rougher flotation with MIBC/DF250 addition
- Scavenger flotation conditioning with copper sulphate (to activate sulphides)
- Scavenger flotation with application of PAX, MIBC and DF250
- The rougher float concentrate (and the first scavenger float concentrate—not shown on Figure 9) is sent to conditioning followed by three stages of cleaning to produce a final concentrate
- The scavenger flotation concentrate and the first cleaner flotation tailings are reground to 25–30 \( \mu m \) particle size \( P_{80} \) and directed back to the rougher flotation circuit
Keynote address: Hydrometallurgical process development for complex ores
Figure 10—NorthMet process flowsheet: hydrometallurgical treatment of bulk Cu-Ni-Co-Zn-Au-PMG concentrate with production of copper cathode, Au/PMG precipitate and mixed Ni/Co hydroxide
The third cleaner concentrate is thickened and reground to approximately 15 μm particle size (P<sub>80</sub>) and sent to the autoclave feed tanks.

A series of batch and continuous pilot-plant crushing/grinding/flotation tests was performed at SGS-Lakefield as part of the metallurgical development programme. The results of a series of six test periods are summarized in Table VI. The first two sample periods were treating assay reject ‘start-up’ material followed by treatment of a composite (C4). The C4 composite sample was obtained from NorthMet deposit in the area of the first five years of the NorthMet mine life. On average for the four periods in which C4 sample was processed, the results indicate:

- 3.73% mass pull and float recoveries of 89.8% for Cu, 70.5% for Ni, 87.2% for S, 36.2% for Co, 73.3% for Au, 84.7% for Pt and 82.7% for Pd.

A recent series of flotation tests has been performed using two further samples of PolyMet ore at 0.30 and 0.25% Cu head grade with the goal of producing a higher grade bulk concentrate product.

The results of the recent series of tests are encouraging. The mass pull was reduced by cleaning more aggressively and use of a gangue depressant in the cleaning stages. The higher grade bulk concentrate will be separated into copper and nickel rich concentrates using conventional separation methods.

### Autoclave leaching

The autoclave leaching process for NorthMet utilizes a small amount of chloride (approximately 7–10 g/l) in solution under ‘total pressure oxidation’ conditions to extract Cu, Ni, Co, Zn, Au, Pt, Pd from the bulk concentrate. The principles of the PLATSOL® process for NorthMet ore processing have been described elsewhere and will be only briefly reviewed here. The process is regarded as a nominal ‘step-out’ from commercial practice in total pressure oxidation for base and precious metal ore/concentrate treatment.

The autoclave oxidation process converts metal sulphide minerals into metal sulphates and iron hydrolysis products (primarily haematite but some basic ferric sulphate may also form under high acid conditions), while the precious metals are converted to chloro-complexes. The chemical reactions believed to occur in the autoclave are shown below. (Note that the mineralogy of the PGMs may be very complex, but for simplicity only the metallic species are considered.)

Chalcopyrite oxidation/iron hydrolysis:

\[
\text{CuFeS}_2 + 4.25\text{O}_2 + \text{H}_2\text{O} = \text{CuSO}_4 + 0.5\text{Fe}_2\text{O}_3 + \text{H}_2\text{SO}_4
\]

Pyrite oxidation:

\[
\text{FeS}_2 + 3.75\text{O}_2 + 2\text{H}_2\text{O} = 0.5\text{Fe}_2\text{O}_3 + 2\text{H}_2\text{SO}_4
\]

Pyrrhotite oxidation:

\[
\text{Fe}_7\text{S}_8 + 16.25\text{O}_2 + 8\text{H}_2\text{O} = 3.5\text{Fe}_2\text{O}_3 + 8\text{H}_2\text{SO}_4
\]

Nickel sulphide oxidation:

\[
\text{NiS} + 2\text{O}_2 = \text{NiSO}_4
\]

Basic ferric sulphate formation:

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

Gold oxidation/chlorocomplex formation:

\[
\text{Au} + 0.75\text{O}_2 + 4\text{HCl} = \text{HAuCl}_4 + 1.5\text{H}_2\text{O}
\]

Platinum oxidation/chlorocomplex formation:

\[
\text{Pt} + \text{O}_2 + 6\text{HCl} = \text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}
\]

Palladium oxidation/chlorocomplex formation:

\[
\text{Pd} + 0.5\text{O}_2 + 4\text{HCl} = \text{H}_2\text{PdCl}_4 + \text{H}_2\text{O}
\]

The temperature range for total pressure oxidation is typically 220 to 230°C. The autoclave discharge from the leach process contains dissolved Cu, Ni, Co, Zn, Au, Pt and Pd.
The solids are relatively ‘barren’ of value, consisting of iron precipitates, unreacted gangue, and minor amounts of residual base and precious metal minerals.

The original PLATSOL® pilot plant utilized a ‘straight through’ design in which fresh concentrate was introduced into the first compartment of a six-compartment pilot autoclave with raffinate (for controlled cooling of the autoclave slurry) and oxygen (for oxidation). The results of the ‘straight through’ pilot plant indicated that virtually all the copper and nickel were extracted in the first compartment of the autoclave due to the rapidity of the sulphide oxidation process. However, the platinum and palladium minerals continued to react through the entire autoclave volume, reaching ultimate extractions of about 95%. This situation was revisited in the more recent bench and pilot-scale testing. It was concluded that a ‘recycle’ design would be more efficient with respect to autoclave design. The ‘recycle’ design involves thickening the autoclave discharge and recycling a portion of the underflow to the autoclave feed. This recycle allows for any unreacted mineral to have a chance at second-pass extraction. The greater the recycle, the longer the ‘average’ residence time of solids in the autoclave. The limit of the recycle will be when the solids density in the autoclave becomes unmanageable.

Figures 11 and 12 show the impact of solids recycle on base and precious metal extraction. While there is some ‘noise’ in the results, there is a strong indication of improvement in both base and precious metal extraction in applying the recycle system. Nickel extraction improved from 97% extraction to over 98%, whereas platinum and palladium extraction improved from less than 90% to between 90% and 95% overall extraction. Regardless of the recycle ratio, the copper extraction was excellent at over 99%. Gold extraction was highly variable, probably due to the small amount of gold in the feed sample (0.8 to 1.3 g/t), but always around 90%. The method of reporting recycle is mass of recycle solids per mass of feed solids (t/t), expressed as a per cent.

Inspection of the graphs indicates that at least 100% recycle ratio will improve overall metal extractions.

Further insight into the kinetics of the pressure oxidation process can be obtained by taking compartment samples from the autoclave at steady-state. Figure 13 shows the precious
metal solution and solids assays in the compartment samples obtained at 74% recycle ratio. Figure 14 gives the comparable information for the base metals. Note that the feed grades in each case have been diluted with the barren solids recycled from the autoclave discharge.

The results show clearly that even with recycle and a relatively short autoclave residence time of 1.1 hours, the oxidation and extraction of the bulk of the base and precious metals is largely complete within the first two compartments of the autoclave (approximately 22 minutes of the 66-minute residence time). This result is consistent with all other reported information on total pressure oxidation of sulphide concentrates including the developments of Placer Dome and Phelps Dodge on copper concentrate total oxidation.

**Au and PGM precipitation**

The autoclave discharge slurry is partly recycled (after thickening) and partly filtered to advance the metal bearing solution to the downstream recovery steps in the process. The gold and platinum group metals in solution are the first target for recovery using reductive precipitation.

In the first PLATSOL® pilot plant reported in 2001, a combination of sulphur dioxide reduction of ferric ion followed by sulphide precipitation was used to recover the precious metals from the pregnant solution.

In the recent pilot campaign an improved method of precious metal recovery was tested. Copper sulphides produced by precipitation of copper from the bleed stream advancing to nickel and cobalt recovery were utilized for precious metal recovery. The copper sulphides ‘cement’ the precious metals onto the solid surface, resulting in an enriched product to advance to further processing. The improved process was proven to be robust and flexible. It is still advantageous to reduce the ferric species in the advancing solution using sulphur dioxide gas to minimize the CuS demand for Au and PGM precipitation.

**Ferric reduction:**

\[
Fe_2(SO_4)_3 + SO_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4
\]

**Gold precipitation:**

\[
2HAuCl_4 + 3CuS + 3H_2SO_4 = 2Au + 3CuSO_4 + 8HCl + 3S
\]

**Platinum precipitation:**

\[
H_2PtCl_6 + 2CuS + 2H_2SO_4 = Pt + 2CuSO_4 + 6HCl + 2S
\]

**Palladium precipitation:**

\[
H_2PdCl_4 + CuS + H_2SO_4 = Pd + CuSO_4 + 4HCl + S
\]

The recovery of gold, platinum and palladium from the autoclave solution (after filtering and washing the solids) was accomplished by precipitation with CuS in the pilot plant. The precipitate solids are collected in a thickener/clarifier arrangement and then filtered. Recoveries of gold, platinum and palladium into this precipitate concentrate were excellent, in excess of 99.5% in each case. Base metal losses from solution into the PGM and gold residue were negligible.

Approximately 4 kg of precipitate were collected during the 2005 pilot plant analysing 56 g/t Au, 211 g/t Pt and 907 g/t Pd. Most of the precipitate mass was copper (35.7%) and sulphur (49%). Batch releaching of the precipitate to remove copper and sulphur was tested and resulted in an upgraded material analysing approximately 1.6% or 16 000 g/t total contained gold, platinum and palladium. The solution after gold, platinum and palladium recovery advances to base metal recovery. The solution is still acidic and must be neutralized prior to copper solvent extraction.

**Solution neutralization**

The extraction of copper by solvent extraction is inhibited by acid in solution. It is therefore important to neutralize the excess acid from the autoclave process prior to advancing to copper recovery.

The neutralization process was piloted in a three-stage neutralization circuit with limestone slurry for neutralization. The gypsum product is thickened. A 300% recycle of gypsum as ‘seed’ for precipitation was used to grow coarse, clean, crystals of gypsum.

The chemistry of neutralization is shown below.

**Gypsum precipitation:**

\[
H_2SO_4 + CaCO_3 + 2H_2O = CaSO_4.2H_2O
\]

The utilization of carbonate exceeded 99% in the pilot tests due to the use of the 300% recycle. The gypsum product assay is shown below. The chemical quality, physical nature and colour of this synthetic gypsum produced in the pilot
Copper SX/EW

The recovery of copper by SX/EW is conventional technology. The presence of chloride in the feed solution to copper solvent extraction necessitates the application of a wash or scrub step to displace any entrained chloride from the loaded organic solution.

Copper extraction:

\[
\text{CuSO}_4 + 2\text{HR}(\text{org}) = \text{CuR}_2(\text{org}) + \text{H}_2\text{SO}_4
\]

Copper stripping:

\[
\text{CuR}_2(\text{org}) + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + 2\text{HR}(\text{org})
\]

Copper electrowinning:

\[
\text{CuSO}_4 + \text{H}_2\text{O} = \text{Cu} + \text{O}_2(\text{gas}) + \text{H}_2\text{SO}_4
\]

In the pilot plant, copper was extracted in three counter-current stages, scrubbed in one and stripped in two stages with spent electrolyte from the electrowinning cell. Two extractants were evaluated, 35% Acorga M5640 from Cytec in Orfom SX 80CT and 35% LIX 973NS LV from Cognis in the same diluent. Both extractants performed well in the pilot-plant operation. Extractions averaged about 95% from a starting solution concentration of 17.4 g/l of Cu (average). A total of 68 kg of copper were extracted and electrolyzed during the 2005 pilot plant run at a current density of +270 A/m². The copper metal cathode was analysed and found to meet LME grade A copper purity specifications. This product can be sold directly to copper consumers. Table VIII summarizes the assay for copper for two samples taken from the second strip cycle in the pilot plant.

Raffinate neutralization

The purpose of raffinate neutralization is to trim the acid level in the copper raffinate prior to splitting the raffinate flow between the nickel and cobalt recovery circuit and returning the raffinate to the autoclave circuit as a cooling solution. Acid must be neutralized prior to the nickel and cobalt recovery process steps and excess acid is undesirable in the feed to the autoclave as excess acid will increase the formation of basic ferric sulphate in the autoclave solids.

The chemistry of raffinate neutralization is the same as the primary neutralization discussed above.

Fe and Al removal

The removal of iron and aluminum prior to recovery of nickel and cobalt is necessary to prevent product contamination. The process of iron oxy-hydrolysis is well known. Iron is oxidized from the ferrous to the ferric state with oxygen or air with limestone addition for neutralization and pH control. The temperature for iron removal was set to 60°C and the pH to 3.0. The iron was removed to less than 5 mg/l by this process with negligible losses of Ni/Co to the iron precipitate residue.

Similar results were obtained in the pilot plant using limestone to pH 4.6–4.7 and 65°C. Terminal aluminum levels were 38 mg/l on average.

The iron precipitate is washed and disposed to tailings. The aluminum precipitate is thickened and recycled to the iron removal step.

Table VII

<table>
<thead>
<tr>
<th>Gypsum solids assay from neutralization of autoclave acid</th>
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<tbody>
<tr>
<td>Ni %</td>
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<tr>
<td>0.005</td>
</tr>
<tr>
<td>Fe₂O₃ %</td>
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<td>0.06</td>
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<tr>
<td>MnO %</td>
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<tr>
<td>&lt;0.01</td>
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</table>

Dry product P₉₀ – 105 microns, wet PSD determinations using Malvern Mastersizer 2000

*The first strip cathode had higher levels of contaminants. This was attributed to the ‘start-up’ conditions used and the fact that the lead anodes in electrowinning were not conditioned prior to commencement of the pilot plant. The purity of the second strip cathodes is believed to be representative of the full-scale chemistry of the copper cathodes to be produced at NorthMet.

Table VIII

| Copper assays for samples taken from the second pilot plant strip cycle* |
|-----------------------------|-----------------|-----------------|-----------------|-----------------|
| 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  |

*The Journal of The Southern African Institute of Mining and Metallurgy
Copper removal
Residual copper is removed before nickel, cobalt and zinc recovery using NaSH precipitation. The copper sulphide product (synthetic covellite) is then recycled internally to precipitate gold and PGM from the autoclave discharge solution.

The chemistry is straightforward:
$$\text{CuSO}_4 + \text{NaSH} \rightarrow \text{CuS} + 0.5\text{Na}_2\text{SO}_4 + 0.5\text{H}_2\text{SO}_4$$

In the 2005 pilot plant, the copper level in solution advancing to copper removal was reduced to less than 50 mg/l.

Nickel, cobalt and zinc recovery
There were two options for nickel, cobalt and zinc recovery that were continuously piloted at SGS—Lakefield in 2005. The first option utilized a classic ‘mixed hydroxide’ precipitation route for recovery of the pay metals in a single product. The second option was to separate cobalt and zinc away from nickel using solvent extraction, followed by selective stripping of cobalt and zinc. The purified nickel, cobalt and zinc streams can then all be treated with magnesia to recover purified hydroxides (or in the case of zinc, be sold directly into the zinc chemicals industry).

Mixed hydroxide results
The mixed hydroxide process uses two-stage precipitation for nickel and cobalt recovery. In the first stage, approximately 85% of the nickel and cobalt are precipitated with magnesia (MgO). This precipitate is then thickened, filtered and washed and sent to a nickel off-take party. The balance of the nickel and cobalt are then precipitated with lime to form mixed gypsum metal hydroxide precipitate. This precipitate is recycled to solution neutralization to redissolve the precipitated nickel and cobalt.

Zinc in solution will report quantitatively to the final mixed hydroxide precipitate.

Nickel precipitation with magnesia:
$$\text{NiSO}_4 + \text{MgO} + \text{H}_2\text{O} = \text{Ni(OH)}_2 + \text{MgSO}_4$$

Cobalt precipitation with magnesia:
$$\text{CaSO}_4 + \text{MgO} + \text{H}_2\text{O} = \text{Co(OH)}_2 + \text{MgSO}_4$$

Zinc precipitation with magnesia:
$$\text{ZnSO}_4 + \text{MgO} + \text{H}_2\text{O} = \text{Zn(OH)}_2 + \text{MgSO}_4$$

Residual nickel precipitation with lime:
$$\text{NiSO}_4 + \text{CaO} + 3\text{H}_2\text{O} = \text{Ni(OH)}_2 + \text{CaSO}_4.2\text{H}_2\text{O}$$

Residual cobalt precipitation with lime:
$$\text{CaSO}_4 + \text{CaO} + 3\text{H}_2\text{O} = \text{Co(OH)}_2 + \text{CaSO}_4.2\text{H}_2\text{O}$$

Residual nickel precipitation with lime:
$$\text{ZnSO}_4 + \text{CaO} + 3\text{H}_2\text{O} = \text{Zn(OH)}_2 + \text{CaSO}_4.2\text{H}_2\text{O}$$

The mixed hydroxide material is high quality and may be placed with an off-take/refinery partner for final separation into pure nickel and cobalt and by-products. (Table IX.)

Magnesium removal
The NorthMet ore and concentrate contains some magnesium silicate mineralization. During high temperature autoclave leaching of the concentrate, some magnesium is leached. In addition, magnesia is used around the circuit for nickel and cobalt precipitation, which also results in an increase in the magnesium content of recirculating solutions. In order to control the build-up of magnesium in solution, a magnesium removal step (with lime) was introduced into the circuit.

Magnetite sulphate reacts to form magnesium hydroxide and gypsum with lime.

Magnesium precipitation with lime:
$$\text{MgSO}_4 + \text{CaO} + 3\text{H}_2\text{O} = \text{Mg(OH)}_2 + \text{CaSO}_4.2\text{H}_2\text{O}$$

The removal of magnesium is a control for the build-up of magnesium across the circuit. In the pilot plant approximately 50% of the magnesium was precipitated per ‘pass’ with the balance of the magnesium allowed to recirculate in the overall circuit.

The NorthMet project of PolyMet Mining is well advanced and ready to proceed to construction upon receipt of key permits. The NorthMet project will begin with an initial phase of separate copper and nickel concentrate production for sale followed by commissioning of the hydrometallurgical circuit for bulk concentrate leaching.

The PLATSOL™ process will be used for the treatment of the concentrate. The PLATSOL™ process will dissolve all the metals of value to high levels of extraction in an autoclave, followed by a series of precipitation and SX/EW processes for recovery of final metal products. The final products from the commercial plant will include:

- Copper cathode of LME Grade A quality
- Au and PGM precipitate for toll processing
- Mixed hydroxide product containing Ni-Co-Zn
- Synthetic gypsum

The current design basis is for 32 000 short tons of ore per day to be processed through the refurbished Erie plant and a new hydrometallurgical refinery for metal extraction. Figure 15 shows how the hydrometallurgical plant will be integrated with the existing Erie facility.

### Table IX

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moist. %</th>
<th>Ni %</th>
<th>Co %</th>
<th>Cu %</th>
<th>Fe %</th>
<th>Zn %</th>
<th>Al %</th>
<th>Mg %</th>
<th>Ca %</th>
<th>Si %</th>
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<td>0.05</td>
<td>0.76</td>
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<td>0.04</td>
<td>0.03</td>
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</table>
The existing Erie plant has capacity to operate at approximately three times the planned production rate. Expanded production could be supported by existing resources at NorthMet, exploration success or treatment of other known deposits in the area. Expansion beyond the current permit application would involve additional environmental review and permitting.

Conclusions

Hydrometallurgical processing of complex ores and concentrates offers the possibility of unlocking new and valuable mineral deposits for production of metals. Two such developments have been reviewed as examples of what is possible by developing or integrating new science and technology into a process flowsheet. 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. The use of high rate thickener technology permits the separation and washing of a clayey leach residue. The integration of the CSIRO DSX technology for cobalt and zinc separation away from manganese permits recovery of these important by-product metals, vastly improving the economics of the metallurgical treatment of the Boleo ore. The PLATSOL™ process has opened the way to treat the NorthMet ore of PolyMet mining. Small additions of chloride to total pressure oxidation leaching conditions allows for direct extraction of small concentrations (but economically significant) of platinum, palladium and gold. This novel leaching process, when combined with known methods of copper, nickel/cobalt and precious metal recovery have permitted the development of a hydrometallurgical process for treatment of the NorthMet ore.

Acknowledgements

The author’s education in metallurgical process development began many years ago with W. Charles Cooper (PhD supervisor) and E. Peters (PDF supervisor). In the case of the Boleo and PLATSOL™ developments, extensive collaborative work has occurred with colleagues at SGS Lakefield Research, Bateman Engineering, CSIRO and others. The technical work presented in this paper is a reflection of the combined efforts of many people in various roles moving from early testing and concepts through to final feasibility for each of the process developments.

References