NICKEL AND COBALT RECOVERY FROM MESABA CONCENTRATE

By

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* CESL focuses on sustainable external and internal growth opportunities, technology transfer and improvement projects. Growth opportunities are pursued through the potential application of our proprietary hydrometallurgical technology and the development of novel process designs. Located in Richmond, Canada

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1. ABSTRACT

CESL has developed a hydrometallurgical process for treating Copper and Nickel sulphide concentrates, including bulk concentrates. Both Cu and Ni are leached efficiently into solution, using a proprietary pressure oxidation process, along with other base metals, notably Co. CESL developed the technology in 2001-02 using a low grade Cu-Ni bulk concentrate sample from an undeveloped property owned by Teck in Minnesota, USA called Mesaba. Ni and Co recovery from the leached solution was contemplated at the time, but not finalized. This paper will describe the latest work at CESL on Ni and Co recovery from a recent concentrate obtained from the same ore body. A discussion is also presented regarding the required impurity removal steps and quality of the final mixed hydroxide product.

2. INTRODUCTION

PROJECT BACKGROUND

The Mesaba Copper-Nickel Project of Teck Resources is one of several copper-nickel sulphide deposits within the Duluth Complex of Northern Minnesota. The deposit contains a geologic resource in excess of 1 billion tonnes at approximately 0.43% Cu and 0.09% Ni with minor Co and PGM values. This region consists of several large Cu-Ni deposits. Access and infrastructure (power, road, rail and the town of Babbitt) is excellent as the property is located immediately adjacent to Cliffs’ Northshore Iron Ore Mine.

![Figure 1: Location of Teck’s Mesaba Property](image)

The mineralogy of the Mesaba ore does not allow for effective production of separate copper and nickel concentrates, however, a low grade bulk concentrate may be produced with reasonable copper and nickel recoveries. Due to the capability of the CESL Process to handle bulk concentrates, Teck Resources initiated studies to determine the amenability of the Mesaba bulk concentrate samples to hydrometallurgical testing.

PREVIOUS TESTING ON THE MESABA CONCENTRATE

In September 2001, CESL started performing pilot plant work on the bulk Mesaba concentrate. The results from this campaign have been documented previously [1] and will only be briefly reviewed.
Considerable work went into developing the copper portion of the flow sheet, and by January 2002 it had been decided that Process 4 version of the CESL Process (leaching of all metals in the autoclave without the need for a second stage leach) provided the best results. While the leached copper was recovered effectively using traditional SX/EW technology, recovery of nickel and cobalt from the leach solution was examined, but the flow sheet was not finalized.

In 2002, the scope of the Mesaba project was redefined from making refined nickel and cobalt metal products, to the production of a nickel – cobalt intermediate hydroxide product via precipitation with lime and subsequent elutriation. The decision to produce an intermediate for Mesaba simplified the nickel flow sheet by keeping the solution in a sulphate matrix and thus did not require ammoniacal circuits. The flow sheet was operated at pilot scale from February through July 2002. The design basis for the pilot plant was 1.3 kg/d nickel to a mixed hydroxide intermediate.

Table 1 outlines the key results from the pilot testing program.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Result</th>
<th>Parameters</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper Extraction</td>
<td>95.4%</td>
<td>Gross Oxygen Ratio</td>
<td>0.21</td>
</tr>
<tr>
<td>Nickel Extraction</td>
<td>90.8%</td>
<td>Autoclave Solids Density</td>
<td>235 g/L</td>
</tr>
<tr>
<td>Sulphur Oxidation</td>
<td>5.2%</td>
<td>Autoclave Retention Time</td>
<td>60 min</td>
</tr>
</tbody>
</table>

In the fall of 2002, the Mesaba Project was delayed due to exceptionally low metal prices. Due to an emphasis on other projects, minimal nickel process development work at CESL occurred over the next five years.

3. STAGED CESL NICKEL PROCESS DEVELOPMENT

Further development of the CESL Nickel Process, specifically the purification and recovery stages, was initiated beginning in 2006. This was driven by both a renewed interest in the Mesaba property as an economically viable copper-nickel deposit, and also by attractive nickel prices which predominated at the time.

The development of the nickel purification and recovery flow sheet for the Mesaba concentrate was divided into six distinct stages, with each stage having its own objective. A brief description of each stage is presented in Table 2.

<table>
<thead>
<tr>
<th>Project Stage</th>
<th>Project Description</th>
<th>Objective</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bench Scale</td>
<td>Develop metallurgy &amp; evaluate OPEX</td>
</tr>
<tr>
<td>2</td>
<td>Semi-Continuous Process Optimization</td>
<td>Confirm flow sheet, metallurgy, METSIM</td>
</tr>
<tr>
<td>3</td>
<td>Scoping Study</td>
<td>Confirm economics</td>
</tr>
<tr>
<td>4</td>
<td>Marketing Study</td>
<td>Determine intermediate payable metal value</td>
</tr>
<tr>
<td>5</td>
<td>Pilot Decision</td>
<td>Pilot construction</td>
</tr>
<tr>
<td>6</td>
<td>Pilot Scale</td>
<td>Mass balance, prove metallurgy, produce marketing &amp; environmental samples</td>
</tr>
</tbody>
</table>

In designing the nickel recovery circuits that comprise the Mesaba flow sheet, a review of the previous 2001-2002 Mesaba pilot plant campaign was performed to see if opportunities existed for optimizations.
and improvements. During the 2001-2002 campaign, a bleed of raffinate from Cu SX fed the nickel plant. The simplified nickel plant consisted of the following circuits as illustrated below:

![Diagram of Nickel Recovery Circuits](image)

**Figure 2: 2001-02 Mesaba Nickel Recovery Circuits**

This flow sheet produced a low-grade mixed Ni/Co hydroxide which contained elevated calcium tenors. When flow sheet development restarted in 2006, this intermediate nickel product was not anticipated to be a saleable product due to the impurity levels and low nickel grade.

With aggressive worldwide development of nickel laterite properties around the world early in the twenty-first century, many references became available on process development for nickel properties that faced similar challenges for impurity removal from acid leach streams and the production of saleable nickel products. Of the hydrometallurgical plants, most flow sheets produced a solid nickel intermediate prior to metallic nickel production. There was no particularly favored intermediate amongst the flow sheets investigated—mixed Ni/Co sulphides, mixed hydroxides, and mixed carbonates were all seen. Each intermediate was suited to a particular refinery flow sheet. Sulphides are suitable for processing in smelters and hydrometallurgical refineries and also minimize co-precipitation of certain impurities such as iron, aluminum, and manganese. Hydroxides and carbonates are most suited to hydrometallurgical refineries which could involve either ammoniacal or acid leaching to resolubilize the nickel and cobalt. Subsequent investigations indicated that some pyrometallurgical facilities could also accept mixed hydroxides as a feed, in part because of recent modifications to equipment and processes in anticipation of an increasing world supply of nickel intermediate products from new mine sites.

The industrial production and marketing trends assisted in the definition of a nickel bleed flow sheet that was developed from bench evaluations, progressing to small scale semi-continuous mini-pilot operations, and culminating in a fully continuous pilot campaign.

**BENCH TEST WORK – NICKEL BLEED CIRCUIT EVALUATIONS**

Bench work was commenced to evaluate possible unit operations within a flow sheet that would produce a saleable solid nickel intermediate as a product. This flow sheet was designed for leach solution from Mesaba concentrate (specifically a bleed of raffinate from copper solvent extraction) which was expected to contain 20-40 g/L nickel with significant levels of iron, aluminum, zinc, copper, and cadmium as primary impurities. Synthetic Mesaba leach solution (based on the 2002 pilot campaign data) was prepared and used for bench test work which evaluated the performance of the following impurity removal circuits:

- Iron/Aluminum Removal
- Zinc/Copper/Cadmium Removal
- Nickel/Cobalt Product Precipitation

The impurity removal circuits were required to remove impurities to a level that the resulting mixed nickel/cobalt product would be saleable with minimal treatment penalties. Other requirements of the impurity removal circuits were to achieve acceptably low nickel losses from the plant, minimize nickel recycles within the plant and minimize operating and capital costs.

The product precipitation stage needed to be able to selectively precipitate nickel and cobalt in the presence of impurities such as calcium, magnesium, sodium and manganese. Other challenges in the production of the mixed nickel product were selection of an intermediate product with mixed hydroxides, mixed sulphides and mixed carbonates as the primary options.
Key Findings:

• Iron and Aluminum Removal should be performed in two stages to minimize the recirculating load of nickel. Co-precipitation of nickel with Fe/Al leads to high nickel losses if performed in one stage at pH 5.0 and 40°C. Nickel loss in the second stage at pH 5.0 is dependent on the Al concentration in the feed to that stage because of co-precipitation. At the pH of the second stage, nickel precipitation was found to correlate directly with the aluminum concentration in the feed solution. This effect was illustrated with aluminum spiking tests during bench test work (see Figure 3).

![Figure 3: Effect of Al in Feed Solution on Ni Precipitation in Al Removal](image)

• Sulphide Precipitation could selectively precipitate copper, cadmium and zinc to below 1 mg/L with less than 0.2% Ni co-precipitation.

• An evaluation was performed to determine whether to produce a mixed Ni-Co hydroxide or sulphide at Mesaba. It was decided that a mixed hydroxide would be produced as it would result in lower up-front risk (startup costs and safety) and is suitable for the leach process liquor (i.e. low Mn), but came with a greater back-end risk (marketing). The decision was, in part, influenced by the potential for future on-site refining using the CESL Nickel Process.

• Several types of magnesia were tested for mixed hydroxide precipitation with varying degrees of reactivity and contained impurities. From a leach liquor containing 20 g/L Ni, a magnesia utilization of 93% could be obtained while precipitating 95% of the nickel.

• Manganese removal prior to MHP was a technical success using a variety of process routes. However, an economic review of the process’s feasibility excluded it from the final process flow sheet.

MESABA SEMI-CONTINUOUS TESTING

Based on the 2007 bench results, a semi-continuous nickel plant was constructed and operated in Q4-2007 through Q1-2008. The objective of the mini-pilot plant was to have a defined flow sheet for the Mesaba pilot plant operations scheduled for the fall of 2008. Process solution generated from the Mesaba concentrate confirmed a conceptual nickel flow sheet for Mesaba, which consisted of the following unit operations: Iron and Aluminum Removal, Sulphide Precipitation, Mixed Hydroxide Precipitation (with magnesia), Nickel Scavenging, and Magnesium Precipitation.
Key Findings:

- Limestone precipitation stages for iron and aluminum removal would precede the sulphide precipitation stage as there was a clear correlation between copper concentration in the feed solution and subsequent iron precipitation (see Figure 4).

![Figure 4: Effect of Copper Tenor in Feed Solution on Iron Precipitation](image)

- Pressure filtration was a critical parameter for the successful operation of sulphide precipitation. Negative pressure filtration (i.e. pan filters) passed air over the filters resulting in unwanted 1-2 mg/L Zn re-dissolution.

- Three different MHP flow sheet configurations were tested during semi-continuous testing. The flow sheet variations were implemented with the objective of maximizing magnesia utilization and MHP nickel grade, while attempting to minimize manganese precipitation. A basic illustration of the three flow sheets is provided in Figure 5. Flow sheet C was chosen for use in the pilot plant campaign as it produced a product at the required specifications at reduced capital.
### MESABA INTEGRATED PILOT PLANT CAMPAIGN

Based on the success of the semi-continuous testing, an integrated Mesaba Copper-Nickel pilot plant operated for a three month period. The major objectives of the operations were to:

- Confirm and improve upon process metallurgy;
- Confirm flexibility of the CESL flow sheet by processing Mesaba bulk concentrates at varying mineralogical composition and grade;
- Operate plant in a fully integrated manner ensuring all recycles were continuous;
- Produce Ni-Co intermediate samples for potential customers;
- Collect environmental samples for long-term residue stability testing; and
- Optimize and collect solid-liquid separation engineering data.

The simplified nickel pilot plant consisted of the following circuits as illustrated below:

**Figure 5: MHP Flow Sheets Tested**

<table>
<thead>
<tr>
<th>FLOWSHEET A</th>
<th>FLOWSHEET B</th>
<th>FLOWSHEET C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphide Precipitation Product</td>
<td>Sulphide Precipitation Product</td>
<td>Sulphide Precipitation Product</td>
</tr>
<tr>
<td>MHP Stage 1</td>
<td>MHP Stage 1</td>
<td>MHP Stage 1</td>
</tr>
<tr>
<td>Ni(OH)₂, Co(OH)</td>
<td>Ni(OH)₂, Co(OH)</td>
<td>Ni(OH)₂, Co(OH)</td>
</tr>
<tr>
<td>MgO</td>
<td>MgO</td>
<td>MgO</td>
</tr>
<tr>
<td>MHP Stage 2</td>
<td>MHP Stage 2</td>
<td>MHP Stage 2</td>
</tr>
<tr>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>MHP Product</td>
<td>MHP Product</td>
<td>MHP Product</td>
</tr>
</tbody>
</table>

**Figure 6: 2007-2008 Mesaba Nickel Recovery Circuits**

The process flow sheet and key findings from the 2008-09 Mesaba pilot plant campaign are discussed in the following section.
4. MESABA CESL REFINERY FLOW DIAGRAM AND PILOT PLANT RESULTS

The final integrated Mesaba flow sheet is presented in Figure 7. The plant processes a bulk concentrate through to copper cathode and a nickel-cobalt hydroxide intermediate.
The following section provides a brief description of the results from the 2008-09 CESL Mesaba pilot plant campaign.

**FEED MATERIAL**

A sample of Mesaba bulk Cu-Ni-Co ore was gathered from the Mesaba property in the fall of 2008. From this sample, nine tonnes of concentrate were produced at the Coleraine Minerals Research Laboratories in Coleraine, Minnesota. Various grades of concentrates were produced; with the following table presenting the concentrate feed composition from three distinct periods of operation.

**Table 3: Concentrate Composition of Bulk Concentrate (2008-09 Mesaba Campaign)**

<table>
<thead>
<tr>
<th>Period</th>
<th>Cu (%)</th>
<th>Ni (%)</th>
<th>Co (%)</th>
<th>Fe (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>13.9</td>
<td>1.64</td>
<td>0.08</td>
<td>26.7</td>
<td>21.3</td>
</tr>
<tr>
<td>B</td>
<td>19.0</td>
<td>2.30</td>
<td>0.10</td>
<td>30.6</td>
<td>26.2</td>
</tr>
<tr>
<td>C</td>
<td>21.7</td>
<td>2.36</td>
<td>0.10</td>
<td>31.6</td>
<td>28.7</td>
</tr>
</tbody>
</table>

The mineralogy of the 2008 concentrate sample was considerably different to that processed at CESL in 2001, with an average chalcopyrite to cubanite ratio of 1.8. The change in mineralogical composition was due to a different sampling location of the bulk ore sample, which enabled further examination of the leaching characteristics of concentrate produced from a different area of the deposit. The following table presents the mineralogical composition of the concentrate processed in 2001 and the high-grade concentrate processed during period C of the 2008-09 campaign.

**Table 4: Mesaba Concentrate Mineralogy**

<table>
<thead>
<tr>
<th>Concentrate</th>
<th>Chalcopyrite (%)</th>
<th>Cubanite (%)</th>
<th>Pentlandite (%)</th>
<th>Bornite (%)</th>
<th>Pyrrhotite (%)</th>
<th>Gangue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2001</td>
<td>10</td>
<td>45</td>
<td>5</td>
<td>Trace</td>
<td>5</td>
<td>35</td>
</tr>
<tr>
<td>2008</td>
<td>50</td>
<td>28</td>
<td>7</td>
<td>0.30</td>
<td>2</td>
<td>12</td>
</tr>
</tbody>
</table>

**PRESSURE OXIDATION**

One of the key unit operations in the CESL Process is Pressure Oxidation (PO) in an autoclave, where the copper and nickel sulphide minerals are oxidized to form soluble forms of copper and nickel. During Pressure Oxidation the primary objective is to maximize metal extraction while minimizing sulphur oxidation.

The copper in the Mesaba concentrate is mainly contained in chalcopyrite and cubanite. The oxidation reactions of these minerals are shown below:

\[
12 \text{CuFeS}_2 + 15 \text{O}_2 + 12 \text{H}_2\text{SO}_4 \rightarrow 12 \text{CuSO}_4 + 6 \text{Fe}_2\text{O}_3 + 24 \text{S}^\circ + 12 \text{H}_2\text{O}
\]

\[
\text{CuFe}_2\text{S}_3 + 2 \text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{Fe}_2\text{O}_3 + 3 \text{S}^\circ + \text{H}_2\text{O}
\]

The nickel in the Mesaba concentrate is mainly contained in pentlandite, with the oxidation reaction of pentlandite shown below:

\[
8 (\text{Ni,Fe})_3\text{S}_8 + 45 \text{O}_2 + 36 \text{H}_2\text{SO}_4 \rightarrow 36 \text{NiSO}_4 + 18 \text{Fe}_2\text{O}_3 + 36 \text{H}_2\text{O} + 64 \text{S}^\circ
\]

Pyrrhotite in the concentrate is oxidized almost quantitatively to hematite and elemental sulphur, without any sulphate formation. This reaction is very fast, has only a minor effect on the overall processing.
cost, and generates an ideal “gangue” material or dilution mineral for the concentrate. The oxidation of pyrrhotite is shown below (for simplicity, it is assumed that the iron to sulphur ratio is one):

\[ 4 \text{FeS} + 3 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3 + 4 \text{S}^0 \]

In addition to the sulphide minerals, 5-10% of the elemental sulphur oxidizes:

\[ 2 \text{S}^0 + 2 \text{H}_2\text{O} + 3 \text{O}_2 \rightarrow 2 \text{H}_2\text{SO}_4 \]

The entire plant process liquor inventory has a chloride concentration of approximately 8-12 g/L. The chloride increases reaction kinetics in the autoclave and works as a catalyst to ensure complete oxidation of the sulphide minerals, whilst minimizing sulphate formation.

There are two main feed streams to the Pressure Oxidation autoclave: acid feed and concentrate slurry. The acid feed solution, which is made up of Mg Removal product and recycled acid in the copper SX raffinate, is stored in the acid feed tank. The concentrate slurry is fed to the autoclave from the PO slurry feed tank.

After a retention time in the autoclave of 60 minutes, at 1,380 kPag and 150 °C, the slurry is depressurized in one flash stage. The letdown brings the contents to atmospheric pressure and a temperature of 95-100 °C.

Operating conditions in the Pressure Oxidation circuit were based on results from the 2001-02 Mesaba Campaign.

**Metal extraction**

To determine if there was an opportunity to increase nickel extraction from the Mesaba concentrate, bench leach tests were performed that evaluated several operating parameters. It was determined that the acid feed Ni tenor impacts overall nickel extraction; where an increased re-circulating load of nickel suppressed overall extraction. This effect is illustrated in Figure 9, where the effect of nickel concentration in the PO acid feed is graphed versus the nickel content of the residue for a concentrate containing less than 100 ppm Ni. An increase in the acid feed nickel tenor from 10 g/L to 40 g/L increased the residue nickel content from 0.04% to 0.12%. This suggests that a higher concentration re-circulated to the autoclave may lead to increased nickel losses due to adsorption into the residue. Based on this data and a sulphate balance generated from the Mesaba Metsim model, the design for the Mesaba pilot plant was 24 g/L nickel in the acid feed liquor.

![Figure 8: Mesaba Pressure Oxidation Flow Sheet](image)
The following table presents the key metallurgical results from the Mesaba pilot plant campaign. The results confirm the bench findings that decreasing the re-circulating load of nickel would increase nickel extraction.

Table 5: Key Metallurgical Results from 2008-09 CESL Pilot Test Program

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper Extraction</td>
<td>95%</td>
</tr>
<tr>
<td>Nickel Extraction</td>
<td>95%</td>
</tr>
<tr>
<td>Cobalt Extraction</td>
<td>97%</td>
</tr>
<tr>
<td>Sulphur Oxidation</td>
<td>6.9%</td>
</tr>
</tbody>
</table>

Sulphur oxidation is defined as the percentage of sulphur in the concentrate that is oxidized to sulphate. The amount of sulphur oxidized affects numerous aspects of the flow sheet, and low sulphur oxidation is usually desirable. Most importantly, the sulphur oxidation has a large impact on the autoclave heat balance, and subsequently the autoclave size and all associated equipment. In addition to the effect on capital, the amount of sulphur oxidation affects the overall autoclave oxygen consumption, as well as the amount of acid and soluble iron that must be neutralized with limestone.

COPPER SX/EW

The Solvent Extraction (SX) circuit is the purification step in the CESL copper flow sheet. The SX circuit enables the production of high purity cathode copper in electrowinning by selective ion transfer of copper from a pregnant leach solution (PLS) to a copper electrolyte. Numerous commercial applications of this process exist, and the technology is well proven.

Mesaba operations require two extraction circuits, 3° and 4°. The purpose of each of the extraction steps is as follows:

- The 3° SX circuit extracts most of the copper leached in the PO circuit. Of the resultant raffinate, 80% is recycled to the autoclave and 20% is sent to 3° Neutralization.
- The 4° SX circuit processes the solution that feeds the nickel purification and recovery circuits. The circuit targets a low raffinate copper tenor to minimize copper losses.
During operations, the 4° SX partially loaded organic (pLO) was fed to the 3° SX circuit to fully load the organic stream. Any iron loaded on the partially loaded organic stream was crowded off by fully loading the organic with copper. A simplified schematic of the SX flow sheet is presented in Figure 10.

![Figure 10: Mesaba Copper SX and EW Flow Sheet](image)

During the campaign, 1245 kg of copper cathode were produced at a current efficiency of 96.8%.

**NEUTRALIZATION**

The Neutralization circuit processed 20% of the 3° raffinate stream prior to advancing to the nickel and cobalt purification and recovery circuits. The purposes of this stage are to remove sulphuric acid (H₂SO₄) from solution with limestone and to re-leach nickel and cobalt metal hydroxides recycled from the Nickel Scavenging and Aluminum Removal circuits. The composition of the gypsum produced in 3° Neutralization is shown in Table 6 below.

<table>
<thead>
<tr>
<th>Cu (%)</th>
<th>Ni (%)</th>
<th>Fe (%)</th>
<th>Al (%)</th>
<th>Ca (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0.09</td>
<td>0.03</td>
<td>22.3</td>
<td>17.3</td>
</tr>
</tbody>
</table>

The gypsum produced was virtually free of contaminants, indicating that all elements within the Nickel Scavenging and Aluminum Removal recycles were re-leached into solution. These recycles, along with a 2 hour retention time and the internal recycle of thickener underflow, resulted in 99.2% limestone efficiency.

The addition of Nickel Scavenging and Aluminum Removal recycles to the 3° Neutralization provides a mechanism whereby potential losses of valuable metals are recovered through re-leaching. Table 7 shows the recirculating load of various metals within the nickel plant.
Table 7: Re-circulating Loads’ of Various Metals from Nickel Clean Up and Aluminum Removal Recycles

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Co</th>
<th>Al</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Si</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.07</td>
<td>1.03</td>
<td>2.34</td>
<td>2.28</td>
<td>1.17</td>
<td>1.15</td>
<td>1.54</td>
<td>1.10</td>
</tr>
</tbody>
</table>

*mass in product solution / mass in initial solution

From the ratios, it can be seen that there is twice as much iron and aluminum in the 3° Neutralization product stream as a result of these metals re-leaching. Nickel, cobalt and zinc also re-leach, representing a recovery of valuable metals.

**Fe and Al REMOVAL**

Iron and aluminum are removed from solution to less than 5 mg/L in a two-stage precipitation circuit. The impurities are removed to minimize contamination of the MHP product and to minimize magnesia consumption.

Each stage has a 2-hour residence time and operates at 40°C. The pH is controlled using limestone powder to a pH of 3.7 in stage 1 and 5.0 in stage 2. The residue solids from the first stage contain the bulk of the iron and aluminum with minimal nickel and cobalt values, and are a waste stream from the process.

A stepwise improvement in the stage 1 solids settling and filtration rates was seen at elevated recycle ratios. As shown in Figure 11, with minimal solids recycle, gypsum particles settled first followed by iron hydroxide particles producing two layers of solids at the bottom of the settling cylinder. With an elevated solids recycle, a homogeneous sludge was formed as the iron hydroxide seeded onto the gypsum crystals.

![Figure 11: Left – gypsum and metal hydroxide layers; right – homogenous sludge](image)

The second stage of Fe/Al Removal can tolerate some nickel loss for the sake of MHP product quality as the residue solids are recycled to 3° Neutralization. The recirculating load of nickel, cobalt and copper in the thickener U/F is included in Table 8 as determined by the mass balance. Note that recycling the copper improves overall copper recovery within the plant as the 3° Neutralization product feeds 4° SX.
Table 8: Recirculating Load of Metals from Fe/Al Removal Circuit Stage 2

<table>
<thead>
<tr>
<th>Metals Department</th>
<th>Metal Precipitated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>7%</td>
</tr>
<tr>
<td>Cobalt</td>
<td>3%</td>
</tr>
<tr>
<td>Copper</td>
<td>79%</td>
</tr>
</tbody>
</table>

SULPHIDE PRECIPITATION

Zinc, copper, and residual cadmium are precipitated selectively with hydrogen sulphide gas prior to Mixed Hydroxide Precipitation. The circuit effectively removed copper, cadmium and zinc to target levels of <1ppm, while averaging 0.15% nickel co-precipitation.

The solids in Sulphide Precipitation had a typical zinc grade in excess of 40% (see Table 9). Preliminary discussions indicate that these solids may be marketable to a third party.

Table 9: Sulphide Precipitation Solid Composition

<table>
<thead>
<tr>
<th>Ca (%)</th>
<th>Cd (%)</th>
<th>Co (%)</th>
<th>Cu (%)</th>
<th>Ni (%)</th>
<th>S (%)</th>
<th>Zn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.72</td>
<td>0.53</td>
<td>0.58</td>
<td>10.0</td>
<td>1.4</td>
<td>33.0</td>
<td>43.4</td>
</tr>
</tbody>
</table>

MIXED HYDROXIDE PRECIPITATION

Nickel and cobalt are recovered from the process solution through the addition of calcined magnesia. The MHP circuit consisted of five cascading reactors that operated at 50°C.

Magnesia addition to the circuit is primarily based on stoichiometric addition, with secondary process control being aqueous nickel assays and the pH of reactor five. As shown in Figure 12, at varying magnesia dosages, the pH in reactor 5 correlates well with the product solution nickel tenor. The correlation between the product nickel tenor and reactor 1 pH indicates that higher concentrations of nickel left in the product stream are predictable through pH control, but becomes difficult when the nickel tenor is less than 1 g/L.
Figure 12: pH in Reactor 1 & 5 vs. Product Solution Nickel Concentration

Figure 13 presents the MHP circuit reactor profiles at a 4.1 hour retention time. Precipitation of nickel is rapid with most of the precipitation occurring in reactor 1 and slowing between reactors 2 and 5; manganese precipitation was relatively linear with time. Overall magnesia utilization through the circuit is 96%.

Figure 13: MHP Reactor Profile at a 4.1 h Retention Time

The composition of the MHP solids produced during the campaign is shown in Table 10. The high-quality MHP product will be sold to a third party refinery. Note that arsenic, cadmium, and chromium tenors were all less than the detection limit.
Table 10: Average MHP Composition from Mesaba Pilot Plant Campaign

<table>
<thead>
<tr>
<th>Ni (%)</th>
<th>Co (%)</th>
<th>Mg (%)</th>
<th>Ca (%)</th>
<th>Cu (%)</th>
<th>Fe (%)</th>
<th>Mn (%)</th>
<th>Zn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>46.0</td>
<td>2.0</td>
<td>0.8</td>
<td>0.6</td>
<td>0.02</td>
<td>0.10</td>
<td>0.68</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Operating the MHP circuit with a solid recycle ratio of 200% increased magnesia utilization and nickel grade, as well as improved the settling and filtration characteristics of the solids.

**NICKEL SCAVENGING**

In order to minimize impurities such as manganese and magnesium in the MHP intermediate, a residual tenor of nickel and cobalt was left in the MHP product solution. The Nickel Scavenging stage precipitates these metals with hydrated lime and recycled them back to 3° Neutralization. Overall recovery of nickel and cobalt within this circuit was greater than 97%.

**MAGNESIUM REMOVAL**

Magnesium is both leached from the concentrate in Pressure Oxidation and added via magnesia in the Mixed Hydroxide Precipitation circuit. The purpose of the Magnesium Removal circuit is to bleed magnesium from the process yet leave enough magnesium to support the chloride to minimize the formation of calcium chloride complexes.

Hydrated lime is used to precipitate magnesium, with the product solid sent to tailings for disposal. In the pilot plant, 65% of the magnesium was precipitated per pass with the remainder recycled to PO.

5. CONCLUSIONS

The application of the CESL Process to the Mesaba property is being examined due to difficulties in the production of saleable concentrate(s). Extensive pilot plant testing has shown extractions in excess of 95% for both nickel and cobalt, with overall nickel recovery of 98% from the leach liquor. The low autoclave sulphur oxidation allows for economic recovery of metals from a bulk concentrate.

During the pilot campaign, a saleable mixed nickel/cobalt hydroxide intermediate product was produced that exceeded the grades modeled from bench testing. Samples of the intermediate were sent out for marketing purposes to various third party refiners.

A suite of Mesaba residues were collected throughout the fully integrated pilot plant campaign for residue stability testing.

With the campaign complete, CESL continues to support the advancement of the Mesaba Project. A scoping study is underway and is scheduled for completion later in 2009.

6. REFERENCES