EARLY COPPER PRODUCTION RESULTS FROM VALE’S HYDROMETALLURGICAL CESL REFINERY

By

Jennifer Defreyne¹, Tobias Cabral²

¹ Cominco Engineering Services Ltd. (CESL)
² Companhia Vale do Rio Doce (Vale)

Presented By

Jennifer Defreyne
jennifer.defreyne@teck.com

CONTENTS

1. INTRODUCTION........................................................................................................2
2. COMMISSIONING ....................................................................................................5
3. METALLURGICAL RESULTS ................................................................................8
4. PLANT STATUS....................................................................................................12
5. MORE INFORMATION ABOUT UHC .................................................................12
1. INTRODUCTION

BACKGROUND

Cominco Engineering Services Ltd. (CESL) formed the Refined Metal Project in 1992 with the express purpose of developing an economically attractive hydrometallurgical alternative to the smelting of copper sulphide concentrates. Since the inception of this project, the scope of work has been expanded to include process development on nickel, cobalt, and zinc sulphide concentrates, as well as precious metal recovery from these concentrates when warranted.

Companhia Vale do Rio Doce (Vale) approached CESL in 1997 to evaluate the CESL process on ore bodies that Vale had in its portfolio and specifically the undeveloped high fluoride Salobo deposit in the state of Pará, Brazil. Vale evaluated several hydrometallurgical processes to develop this deposit and the CESL process was selected for a number of reasons, including:

- The process is relatively unaffected by the copper grade of the concentrate. This flexibility allows concentrate copper grade reduction from 38% to 23%, with enormous simplification to the flotation process flow sheet and operation, resulting in lower operating costs and higher recoveries in the concentrator (as high as 4% additional recovery for copper and gold).
- The process achieves high copper recovery.
- The process is environmental friendly compared to alternative pyrometallurgy processes.
- The process is in an advanced stage of development, having treated a number of copper concentrates in a large-scale demonstration plant as well as in a smaller pilot plant.
- A process installation would consist mainly of conventional processing equipment and well-known unit operations.
- The oxidation of sulphur contained in the concentrate is limited, resulting in low oxygen consumption, which reduces the production of acid and consequently reduces neutralization costs.
- Gold can be recovered from the waste leach residues by conventional methods (roasting and cyanidation) or by the recently developed CESL hydrometallurgical process.
- The CESL process is one of many hydrometallurgical processes that can treat high impurity concentrates in an economic and environmentally sustainable manner.

After extensive testing at the CESL facilities in Vancouver, BC, Vale decided to construct a 10,000 tonnes per year plant to treat copper concentrates from a similar ore body to prove the process on a semi-industrial scale prior to committing to a full production plant of 250,000 tonnes per year. The flexibility of the CESL process, with some variation in capacity, allows processing Salobo concentrate in the same facility.

Hatch Associates Ltd. completed the Usina Hidro Carajás Feasibility Study in late 2004. Vale approved the UHC project in early 2005 and shortly after, Hatch Associates Ltd. and SEI Consultoria E Projetos S/C Ltd were contracted to begin the basic and detailed engineering for the plant. Under the management of SEI, plant construction began in 2006 and was completed in 2008. The plant is currently operating in an optimization phase, as the commissioning activities were completed in 2008.

PROCESS PLANT DESCRIPTION

The CESL Copper process consists of four main process steps:

- Copper mineral oxidation.
- Copper leaching from the oxidation residue.
- Solvent extraction to produce a high purity electrolyte.
- Electrowinning to recover copper in commercial product form.

Concentrate feed is received at the UHC plant battery limits (Figure 1) and is subjected to a light re-grind in a ball mill (Figure 2) to increase the surface area of the minerals.
The ground concentrate slurry and recycled acid solution are pumped separately into an agitated, five-stage pressure oxidation (PO) autoclave at 150°C and 1,380kPag. Oxygen is added into the first four compartments to achieve oxidation of the copper minerals. Copper is converted from a sulphide mineral to basic copper sulphate (\(\text{CuSO}_4 \cdot 2\text{Cu(OH)}_2\)). Iron present in the copper mineral is oxidized to hematite, and sulphur is converted to elemental sulphur. Very little sulphur to sulphate oxidation occurs, and therefore acid generation is minimal. The copper oxidation reaction is very efficient, occurring in 60 minutes. The presence of chloride in solution (10-12 g/L), which acts as a catalyst for the reactions, is key to the CESL Process autoclave kinetics.

The autoclave final product slurry is discharged continuously through a pressure letdown system. Steam is vented from these tanks, reducing the temperature of the slurry to below boiling. Additional cooling of the discharge slurry is required prior to thickening and filtration; this is achieved by recycling the cooled thickener overflow to mix with the hot autoclave discharge slurry. The cooled autoclave discharge slurry is thickened and filtered (Figure 3). Copper is removed from the autoclave leach liquor by solvent extraction before it is recycled through the evaporator and returned to the autoclave. The evaporator is used to maintain the plant water balance, removing water at a rate of approximately 1.5 m³/hr. The leach filter cake, containing oxidized copper, hematite and elemental sulphur is washed on the belt filter to confine the chloride catalyst to the PO circuit. The washed cake is then repulped with recycled raffinate from solvent extraction (Figure 4) prior to atmospheric leaching. The slurry pH is controlled to a pH of 1.5 using raffinate in the reactor train to efficiently leach the copper from the PO filter cake.
The pregnant leach solution (PLS) from the atmospheric leach is purified using two-stage countercurrent solvent extraction. LIX organic extractant transfers the copper to the electrolyte leaving all of the impurities in the raffinate which is then recycled back to the leach.

Approximately 1/3 of the raffinate is neutralized using limestone to make gypsum. The neutralized solution is then processed through an additional solvent extraction step to remove the copper. This copper-free stream is used to wash the leached residue in a counter-current decantation circuit (CCD).

In the final process step, copper is recovered from the copper rich strip solution produced by the solvent extraction process by conventional electrowinning. The cathode production meets LME Grade A standards.

The main solid waste streams from the plant are the final washed leach residue and gypsum. The final washed leach residue contains the elemental sulphur, hematite and any precious metals present in the concentrate. Figure 5 below shows a simplified version of the UHC process flow diagram.

Figure 5: Simplified Process Flow Diagram
2. COMMISSIONING

A detailed commissioning plan was created to methodically check every piece of equipment, instrument, control and interlock. The goal was to reduce the impact of potential problems which otherwise may have been encountered during first feed. The plan was adjusted to reflect equipment availability, delays, limitations and deficiencies. The following sections detail some of the more interesting commissioning activities and construction issues.

2.1 AUTOCLAVE INSPECTIONS

The first autoclave inspection occurred after approximately one month of consistent operation. There were no signs of wear or undesirable solids accumulation found in the autoclave Figure 6 and 7).

![Figure 6: 1st Autoclave Inspection Compartment 1](image)
![Figure 7: 1st Autoclave Inspection Compartment 5](image)

Upon inspection of the autoclave one month later, a large accumulation of solids (agglomeration of unreacted sulphides and elemental sulphur) were discovered in compartments one and two (Figure 8 and 9). Solids accumulation of this magnitude is not very common and several parameters need to be outside the limits of normal operations for this to occur.

![Figure 8: 2nd Autoclave Inspection Compartment 2](image)
![Figure 9: 2nd Autoclave Inspection Under Agitator](image)

Solids accumulation has been a contributing factor to titanium fires in several commercial autoclaves around the world, and therefore all possible measures must be taken to prevent future accumulations from occurring. Ensuring strict control of the chloride level, temperature, and surfactant level in the autoclave will ensure the sulphide minerals react and the molten sulphur is dispersed, thus preventing the accumulation of solids.
2.1.1 Chloride
Prior to the 2nd autoclave inspection and the discovery of accumulated solids in the autoclave, the chloride level in the acid feed solution was below target, resulting in low copper extraction (estimated at approximately 70%) and the presence of a large amount of unreacted concentrate. This was the major contributing factor to the solids accumulation found in the autoclave. Strict control of the autoclave chloride level (>10 g/L) is needed to ensure adequate copper oxidation and elemental sulphur dispersion. This will prevent future autoclave solids accumulations from occurring.

2.1.2 Temperature
If the temperature in the autoclave increases above 158 C, the viscosity of the sulphur increases exponentially, often leading to the formation of large sulphur globules. As these sulphur globules rarely dissolve under normal autoclave operating conditions, it has become standard practice at CESL’s pilot and demonstration facility to perform an autoclave inspection following temperature excursions >165 C.

2.1.3 Surfactant
A small amount of surfactant is added to the autoclave slurry to act as a sulphur dispersant. This helps keep the molten sulphur as small droplets in the autoclave and prevents sulphur from coating the copper minerals, freeing the minerals to oxidize. Prior to finding the solids, surfactant addition tracking did not occur. After the discovery, a tracking program was instituted to ensure the correct quantity was being added.

2.2 SOLVENT EXTRACTION
The solvent extraction circuit was the most difficult to commission due to the following design and construction issues:

- A lack of aqueous recycle capacity in the extract stages resulted in the inability to maintain target O:A’s in the mixers.
- Insufficient back pressure in the organic lines from the extract and strip stages to the organic tanks led to air locking issues.
- Broken and seized organic weir adjusters caused isolated weir overflows.
- Undersized organic tank heights limited pump head pressures and resulted in challenging pump operation and control.

Each of these issues led to either very high organic entrainments or routine organic spills, resulting in high organic losses. The issues are discussed in more detail in the following sections.

2.2.1 Aqueous Recycle
In a typical mixer-settler design, the piping out of the launder for the recycle flow is well below the piping for the advance flow. As a result, flow out of the launder preferentially occurs in the recycle piping. The impeller speed of that stage or a valve on the recycle line can then be used to control the recycle flow rate to maintain the desired O:A in the mixer.

At UHC, the piping for the recycle and the advance flow out of the launder are at the same level. Since there is less back pressure on the advance flow piping, the aqueous would flow preferentially to the next stage, making it impossible to obtain an aqueous recycle. Target mixer O:A’s could not be achieved, which lead to poor mixing efficiency. In addition, high entrainments were noted because of large velocity differences between the organic and the aqueous in the settlers.

To solve the issue, valves had to be installed on the aqueous advance lines to restrict the aqueous flow, which allowed more flow through the recycle piping. These new valves have to be manually adjusted to achieve the target mixer O:A ratio.

2.2.2 Air Locking in the Organic Piping
During the early stages of commissioning, the loaded and stripped organic lines were operating only partially full. There wasn’t sufficient back pressure in the lines to maintain a level in the launder, which allowed air to get into the piping. This posed both a safety hazard, as well as made operations very difficult. The air would accumulate at the highpoints in the line, eventually air-locking, which would cause frequent organic overflows at the settlers.

To solve this issue, manual valves were installed on the loaded and stripped organic tanks to provide back pressure in the lines and to ensure a level could be maintained in the organic
launders. A series of vents also had to be installed on high points on the lines to allow air to be bled from the piping. The circuit is now functional, but air must routinely be bled through the vent lines and the manual valves at the LO and SO tanks must be adjusted to maintain the desired organic levels in the launders.

2.2.3 Organic Weirs

The organic weir is divided into several sections, each with an independently adjustable baffle. Vertical rods were attached to each end of the baffle and the height adjustment was done by lifting the rods to the proper height and fixing them to the settler frame with a set screw.

When attempting to level the weirs during commissioning, it was noted that several of the weir adjusters were broken (Figure 10), and many of the set screws were seized, making it impossible to level most of the weirs. This caused the organic to overflow only on isolated sections of the weirs (Figures 11 and 12).

![Figure 10: Broken Adjuster](image1)
![Figure 11: Extract Organic Weir](image2)
![Figure 12: Strip Organic Weir](image3)

It is important to have a uniform flow of both aqueous and organic across the weirs. If the flow is not uniform, it effectively reduces the size of the settlers, causing increased entrainments. During commissioning, the channeling within the settlers caused high levels of organic accumulation in both the raffinate tank and the PE tank. The aqueous entrainments were also high, with the coalescer returning large volumes of aqueous solution back to the circuit everyday.

To level the weirs, small holes were cut into each weir and into each metal hanger, and titanium wire was used to attach the two together. The length of the titanium wire was adjusted to level the organic weirs.
2.2.4 Organic Tanks

For ease of construction, the organic tanks were designed similar in nature to the settlers, allowing the same FRP molds to be used by the fabrication shop. As a result, the organic tanks are very short, approximately 1.5 m to 2.0 m in height. Due to the undersized tank heights and the low-density of the organic, the loaded organic tank and stripped organic tank levels had to be controlled above 60% and 70% respectively to provide sufficient head pressure to prevent pump cavitation. Controlling the tanks above the minimum required levels has significantly reduced the operating volumes, resulting in a retention time of only 5 minutes. This has made it extremely difficult for the operators to balance the flows in and out of the tanks. During commissioning, this resulted in several major spills and organic losses. Since then, the operators have become very proficient at maintaining the tank levels between 70% and 90%, but the flow control still requires significant attention.

2.4 RUBBER-LINED AGITATORS

A design flaw existed with all of the plant rubber coated agitators, resulting in impeller corrosion shortly after plant reagent addition. Upon initial installation, the rubber on the agitator hubs and on the blade mounting faces had been cut away, resulting in a metal-to-metal mating surface. The blades were fastened to the hubs using steel bolts, capped with rubber. This unfortunately did not allow for a proper seal and allowed for the process solution to reach the metal on both the hubs and the blades, causing excessive corrosion and in most cases, the blades to fall off.

The new design arrangement maintained the metal-to-metal mate between the hub tab and the impeller blade (Figure 13). But this time, the entire assembly, including the fasteners, was recovered with rubber (Figure 14). This repair procedure solved the corrosion problem.

Figure 13: Agitator Before Final Wrap
Figure 14: Final Rubber Lining Design

3. METALLURGICAL RESULTS

Solutions to most of the major construction issues were identified and implemented late in 2008. At this point in time, plant operations switched from a commissioning phase to production. In December 2008, a major milestone was achieved; the first copper cathode was stripped in electrowinning.

The following sections highlight some of the main metallurgical and production results to date.
3.1 COPPER PRODUCTION

Figure 15 shows the copper cathode production at UHC from December 2008 through March 2009 compared against the monthly ramp-up target.

Between December 1, 2008 and March 31, 2009, just over 1000 tonnes of copper cathode has been produced. Thus far in 2009, the plant has averaged 40% of design.

Significant causes for downtime this year are attributable to inadequate reagent supply, process upsets and pump problems as depicted in Figure 16.

Lack of oxygen has been the largest cause of downtime at UHC. The oxygen is trucked from 1000 km away, making it very difficult to schedule deliveries. Although the plant has three days of
oxygen storage onsite, interruption to supply occurs regularly during poor weather and road conditions leading to extended shutdowns.

Process upsets, namely inventory management issues, have also been a large source of downtime. It has been a very interesting learning experience for all involved in the project as to the troubles of maintaining a water balance during the rainy season in northern Brazil. On a few occasions, the plant has been shutdown and the evaporator used to decrease the volume of process solution to a manageable level.

3.2 COPPER QUALITY

The copper quality in the plant has met our expectations, achieving LME Grade A specifications very early in the project. The following table shows the monthly copper quality up to the end of February.

<table>
<thead>
<tr>
<th>Month</th>
<th>Production</th>
<th>LME Grade A</th>
<th>Standard</th>
<th>Off Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>December 2008</td>
<td>96.1 tonnes</td>
<td>51%</td>
<td>26%</td>
<td>23%</td>
</tr>
<tr>
<td>January 2009</td>
<td>345.2 tonnes</td>
<td>97%</td>
<td>3%</td>
<td>0%</td>
</tr>
<tr>
<td>February 2009</td>
<td>296.0 tonnes</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
</tr>
</tbody>
</table>

In December, a large portion of the first harvest of cathodes was off grade due to lead contamination, which is to be expected after loading anodes into the electrowinning cells. Since the first harvest, quality has been excellent, with 100% meeting LME Grade A specifications by March.

Current efficiency in the tank house has been good, averaging 92-93% to date.

3.3 COPPER EXTRACTION

The main metallurgical concern to date at UHC is that copper extraction has been lower than the design target of 96%. This target was based on several months of pilot and demonstration testing at CESL on Sossego concentrate as well as concentrates from other Vale properties. At this point in time, it has been concluded that the low extraction at UHC is a result of low levels of chloride in solution. The key to the CESL Process is the presence of chloride at 10-12 g/L in the autoclave solution. The chloride catalyzes the oxidation of copper minerals and without target levels in solution, years of testwork at CESL has shown extraction rarely exceeds 85%.

The low levels are a result of two issues:

- The remoteness of the site has made HCl deliveries late by several weeks, making it difficult to co-ordinate regular addition.
- Chloride losses have been approximately 3 times higher than expected.

Figure 17 shows the average UHC copper extraction to date at varying chloride levels.
Copper extraction has ranged from 80% to 93% during the first three months of operation. Vale has recognized the importance of controlling the chloride level and its affect on copper extraction and is focusing on improving the delivery schedule of HCl to site. To minimize future addition requirements, a rigorous sampling campaign will occur in April and May to identify the sources of chloride loss in the plant.

3.4 SULPHUR OXIDATION AND OXYGEN CONSUMPTION

The following table contains the average sulphur oxidation and oxygen consumption results to March 31, 2009.

Table 2: Sulphur Oxidation and Oxygen Consumption

<table>
<thead>
<tr>
<th>Sulphur Oxidation (%)</th>
<th>Gross Oxygen Consumption (kgO₂/kg Con)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>0.37</td>
</tr>
</tbody>
</table>

The theoretical oxygen consumption for the autoclave reactions is 0.28 kgO₂/kg Con. With 20% excess consumption expected, the gross oxygen ration should be closer to 0.34 kgO₂/kg Con. With improved runtime in the autoclave, the oxygen consumption per tonne of concentrate is coming inline with design expectations.

Sulphur oxidation has ranged between 8% and 12% and is directly related to the amount of pyrite in the concentrate. Approximately 75% of the pyrite oxidizes to form sulphuric acid in the autoclave, which accounts for all of the sulphur oxidation. The sulphur in the copper minerals converts to elemental sulphur almost quantitatively.
4. PLANT STATUS

CESL and Vale will continue to work together throughout 2009 to bring the plant to design capacity and gather the required information for the design of a larger CESL refinery. In the short term, focus is on improving copper extraction and plant availability, which are largely related to coordination of reagent deliveries, namely oxygen, flocculent and HCl.

5. MORE INFORMATION ABOUT UHC

N. Hayton, J. Defreyne, “UHC Copper Refinery: An Update on the Vale Project Based on CESL Technology”, HydroCopper 2009 Proceedings, Antofagasta Chile

T. Brace, J. Defreyne, “Commissioning UHC: a CVRD Copper Refinery based on CESL Technology”, Hydrometallurgy 2008 Proceedings, Phoenix USA

A. Omena, J. Geraldo, “Technical Feasibility Study to Produce Cathodes in the UHC Carajas Plant by the Hydrometallurgical CESL Route”, HydroCopper 2007 Proceedings


J. Defreyne, G. Barr, “CESL Copper Process - Moving from Pilot Plant to Production Scale Operation”, Hydrosulphide 2004 Proceedings, Santiago, Chile

Figure 18: Photos of the UHC Copper Refinery