Environmental benefits of the CESL Process for the treatment of high-arsenic copper-gold concentrates

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ABSTRACT
The ongoing development and implementation of hydrometallurgy for the processing of copper concentrates is driven by several factors, including: the increasing trend in global copper consumption, the increasing development of challenged resources (complex mineralogy, lower grade ores, deleterious elements), increasingly stringent environmental and occupational health and safety regulations, and the high cost and limited availability of treatment and refining options for complex concentrates. The traditional method for processing high-arsenic concentrates is blending with large amounts of clean concentrate. This is followed by the traditional processing route of smelting and refining, which results in the generation of an unstable arsenic trioxide product.

Through a partnership formed in 2009 between Teck, Canada’s largest diversified resource company, and Aurubis, a leading custom concentrate refiner and the world’s largest copper recycler, extensive integrated pilot scale tests have been completed using the CESL Process to treat high-arsenic copper and copper-gold concentrates. The key unit operations of the CESL Process are: concentrate regrind, oxidative pressure leach with a chloride catalyst, followed by conventional solvent extraction and electrowinning. For concentrates also containing precious metals, the residue from the CESL Process is processed through a pressure cyanidation circuit followed by a traditional precious metals recovery circuit. The result is a sustainable and cost effective process for the production of high-quality copper cathode and precious metals.

This paper describes the environmental benefits of the CESL Process for the treatment of high-arsenic copper and copper-gold concentrates in comparison to traditional processing routes. The CESL Process provides tangible environmental benefits to water, air, climate and soil such as: decreased fresh water consumption; decreased particulate (as arsenic trioxide) and sulfur dioxide emissions; decreased greenhouse gas emissions; and decreased unstable arsenic species for ground disposal.

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INTRODUCTION

About 80% of the copper ore reserves are found in porphyry deposits and about half of those contain arsenic-bearing minerals (Schwartz, 1995). Approximately 60% of the 306 copper mines in operation today contain some level of arsenic (WoodMac, 2016). Increasing arsenic levels presents an emerging challenge for the mining and smelting industry. Many existing deposits that produced clean concentrates a few years ago are now facing arsenic levels above the penalty limit of 0.2%, as shown in Figure 1.

Two mines that recently started operations, Toromocho (Peru) and Mina Ministro Hales (Chile), are distinguished by appreciable arsenic contents, 1.3% and 3.6% in concentrate, respectively (WoodMac, 2016). Many large development projects such as La Granja (Peru), Quellaveco (Peru), Frieda River (Papua New Guinea), and Cañariaco Norte (Peru) are also reported to contain arsenic (Schwartz, 1995; Candente, 2011).

The global copper smelting industry has limited capacity to treat deleterious elements due to environmental standards and requirements for copper product quality. For example, the Ministry of Environment in Chile established a new policy regulating fugitive emissions of arsenic, sulfur dioxide, particulate matter and mercury from smelters. Existing smelters in Chile need to comply
with emission standards of 95% capture for arsenic and sulfur dioxide, and any new installations have even more stringent emission standards of 99.98% capture for arsenic and 98% for sulfur dioxide (Voisin, 2015). China has imposed limits on arsenic import levels of copper concentrates restricting the import of concentrates containing over 0.5% arsenic.

With the amount of arsenic in concentrates increasing and with environment, occupational health and safety regulations becoming more stringent, there is a need for an alternative processing method. The ideal processing route for high-arsenic copper concentrates would result in no arsenic emissions and would capture all of the arsenic while immobilizing it in a compound that is stable under a wide range of conditions so it is suitable for long-term disposal. The long-term stability of arsenic compounds depends on a number of factors including disposal site characteristics, particle crystallinity and size distribution, the presence of complexing agents and the effect of bacterial activity (Riveros et al., 2001). Compounds containing ferric iron (Fe III) and arsenic in the pentavalent state (As V) are considered to be the most suitable forms for long-term arsenic disposal, specifically as crystalline ferric arsenates such as basic ferric arsenate sulfate (“Type 2 Scorodite”) and scorodite (Demopoulos, 2014).

The CESL Process, developed by Teck and Aurubis, is capable of processing high-arsenic copper and copper-gold concentrates and fixing arsenic as scorodite without generating any particulate or sulfur dioxide emissions. The advantages of, and results from, the CESL Process for the processing high-arsenic concentrates (from 1 to 12% arsenic) have been presented previously (Mayhew, Salomon-De-Friedberg & Lossin, 2016; Salomon-De-Friedberg et al., 2015; Mayhew et al., 2014; Bruce et al., 2011). Results include: production of LME Grade A copper cathode, copper extraction over 97%, copper recovery over 95%, silver extraction up to 95%, gold extraction up to 90%, and arsenic deportment to a stable residue over 99%. The stability of the leach residue from the CESL Process has been demonstrated through short- and long-term testwork. Mineral characterization by X-Ray Diffraction (XRD), Mineral Liberation Analyzer (MLA) and Fourier Transform Infrared Spectroscopy (FTIR) has confirmed the CESL Process residues consist of scorodite and basic ferric arsenate sulfate.

The sustainable processing of high-arsenic concentrates requires a global perspective. The environmental benefits of the CESL Process for processing of high-arsenic copper-gold concentrates were quantified and compared to traditional processing methods as presented in this paper.

**CESL Process**

The major steps of the CESL Process are shown in Figure 2.
Copper concentrates are reground to a p80 of less than 15 microns and subjected to a chloride catalyzed oxidative pressure leach at 150°C and 1380 kPa pressure to favor the precipitation of arsenic as scorodite. Leach retention time is from 60 to 90 minutes to promote complete oxidation of the copper sulfide minerals and maximize arsenic precipitation. Depending upon the slurry pH leaving the autoclave, additional acid may be required in an atmospheric leach to extract further copper. The final residue is washed before long-term disposal or precious metal processing if gold and silver are present.

The combined leach solution and wash water containing 30-60 g/L copper is directed to solvent extraction and electrowinning to recover the copper as cathode. Due to the high copper tenor entering SX, the extractant concentration in the organic is typically 30-40%, which helps keep the iron concentration in electrowinning below 300 ppm. Electrowinning otherwise operates under standard conditions. A portion of the raffinate from solvent extraction is recycled to the leach circuit and another portion can either supply acid to a nearby heap or be neutralized with limestone to maintain the overall sulfate balance. The neutralized solution is recycled to the leach circuit except for a small bleed stream which is treated with lime to remove impurities. An evaporator may be required to maintain the overall water balance, with the condensate being used as wash water, lowering fresh water requirements.

Residue processing for precious metal recovery comprises pressure cyanidation, metal adsorption onto activated carbon, and carbon stripping followed by electrowinning to produce a precious metal sludge. Cyanide-bearing solutions are recycled. Copper and cyanide are recovered from a small bleed stream prior to cyanide destruction. Residue containing minor amounts of copper is directed back to the copper process, improving overall copper recovery.

**Conventional processing – low arsenic concentrates (<1%)**

To reduce the arsenic in copper concentrates to meet smelter thresholds (~0.2% arsenic) and to meet China import restrictions (<0.5% arsenic), miners and traders resort to diluting the impurities below
the threshold levels thus dispersing the arsenic over larger areas and in larger amounts of waste. After blending, the concentrates are traditionally processed by smelting and refining. During smelting, some of the arsenic volatilizes together with sulfur and reports to the flue dusts as sulfide (As₂S₃) or oxide (As₂O₃) while the rest departs to the slag and off-gas. In order to have sufficiently low levels of arsenic in the gas before entering acid plant, the gases are cooled and the majority of arsenic is removed as arsenic tri-oxide (As₂O₃) dust. Since there is a limited market for this and because its high solubility makes it unsuitable for long-term disposal, smelters tend to cycle it through the smelter, thus increasing the overall arsenic levels in the system.

Conventional process – high arsenic concentrates (>1%)

Besides being less than optimal from an economic and environmental perspective, blending is only applicable to concentrates with lower arsenic levels. Blending concentrates containing several percentages of arsenic requires up to twenty times the amount of clean concentrate which may not be available. When the ore body contains areas with high arsenic, either the area is not mined and the metal value is lost or the areas are mined and stockpiled without ever being concentrated and the metal value is again lost. Today, some concentrates with very high arsenic content are processed in a few specialized smelters (e.g. Tsumeb, Shandong Humon), where the arsenic is either disposed of in a lined storage facility or stockpiled for further treatment in its highly soluble and toxic form. Codelco’s Mina Ministro Hales concentrates are roasted to low-arsenic calcine. The arsenic is concentrated into a roaster dust which requires treatment or copper recovery and arsenic fixation but no proven technology is available for long-term disposal. In 2014, EcoMeteles invited several companies to help develop a process to treat the roaster dust; the dust was being stored temporarily at the EcoMeteles site (EcoMeteles Sustainability Report, 2014).

Arsenic Disposal

Historically, arsenic has been disposed as calcium arsenate (e.g. in the majority of effluent treatment plants of the smelters in Chile) and arsenic sulfide (e.g. Lepanto in Philippines and Saganoseki in Japan) (Valenzuela, 2000). These arsenic compounds have not proven to be stable (Riveros et. al, 2001) and with health and environmental focus increasing, new methods for arsenic stabilization are emerging. Co-precipitation with ferric ions is considered the best demonstrated available technology for the removal of arsenic from solution (Rosengrant & Fargo, 1990), with ferric arsenate sulfate (especially as scorodite) being the preferred stable compound for disposal (Demopoulos, 2014). Some plants are using atmospheric precipitation of scorodite, e.g. EcoMeteles, treating Codelco’s flue dusts, and arsenic removal from bleed electrolyte at the Kosaka smelter in Japan (Kubo, 2010). Atmospheric scorodite precipitation is costly due to the oxidizing and energy requirements. There are currently no facilities using pressure leaching processes for the precipitation of scorodite.
METHODOLOGY

Teck and Aurubis contracted Offsetters Clean Technology Inc. to help quantify the environmental benefits of the CESL Process for processing high-arsenic copper-gold concentrates through to copper metal when compared to conventional processing routes. The processing of high-arsenic copper-gold concentrates using the CESL Process at a planned custom refinery in Peru was compared to two baseline scenarios that represent business-as-usual in the industry: 1. high-arsenic copper-gold concentrates are sent for direct smelting to the Tsumeb smelter in Namibia (Baseline 1); and 2. high-arsenic copper-gold concentrates are sent to a blending facility, are blended with low-arsenic concentrates, and the blended concentrate is sent to a smelter located in China (Baseline 2).

A standard life cycle methodology was used to evaluate the environmental benefits of using the CESL Process to treat high-arsenic copper-gold concentrates in a custom refinery in Peru. This involved creating a detailed inventory of all the significant material, energy and water inputs to the processes, as well as discharges of wastes in stack gases, solids and effluents. Two concentrates were evaluated, with the compositions as shown in Table 1.

### Table 1 High-arsenic copper-gold concentrates evaluated for environmental benefits

<table>
<thead>
<tr>
<th></th>
<th>Copper</th>
<th>Arsenic</th>
<th>Iron</th>
<th>Sulfur</th>
<th>Gold g/tonne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate 1</td>
<td>26</td>
<td>8</td>
<td>19</td>
<td>38</td>
<td>2.5</td>
</tr>
<tr>
<td>Concentrate 2</td>
<td>33</td>
<td>4</td>
<td>18</td>
<td>32</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The boundary conditions start from the shipment of the concentrate from a mine in Peru located 250 kilometers driving distance from Lima and end prior to the shipment of copper cathode and precious metals byproducts from the production location (the custom refinery or the smelters).

Assumptions included:
- The custom refinery is located 50 km north of Lima and 110 km from the port
- Transportation environmental impacts post-production are excluded from the analysis
- The use and disposal phases of the copper and precious metals life cycles are assumed to have the same impacts for each scenario and are hence excluded from the analysis
- The smelters in China and Namibia achieve 95% sulfur dioxide emissions capture and 95% arsenic capture (i.e. 5% goes out the stack as an air emission), based on China’s current smelter emission standards for sulfur dioxide and arsenic (95%) and Dundee Precious Metals’ statement of achieving up to 95% capture of sulfur dioxide for the Tsumeb smelter. New smelters may have marginally better capture efficiency, however the assumed capture is for what is considered to be a typical smelter using smelting and gas capture technology
• Arsenic trioxide produced by smelters is bioavailable and water soluble unless treated further
• Over 99% of arsenic fed to the CESL custom refinery ends up in a highly stable residue with short- and long-term stability tests confirming it to be a non-hazardous material
• Input materials to the refinery and smelters (other than concentrate) are transported approximately 100 kilometers
• Energy is sourced from the regional grid except for the smelter in Namibia which is sourced from coal
• The custom refinery has no particulate emissions nor sulfur dioxide emissions
• The custom refinery achieves an extraction of 97-98% copper, up to 95% gold and up to 90% silver; the smelters achieve a recovery of 99% copper and virtually 100% of gold and silver
• Some minor reagent inputs are not included in the analysis as they were considered immaterial to the quantification results; these include HCl and CaCl for the CESL Process

Environmental benefits were quantified in four areas: water (fresh water consumption), air (arsenic trioxide and sulfur dioxide emissions), climate (GHG emissions), and soil (unstable arsenic species).

RESULTS AND DISCUSSION

The environmental benefits of using the CESL Process in a custom refinery in Peru versus the two baseline cases for two high-arsenic copper-gold concentrates are presented in Table 2.

Table 2 Environmental benefits of the CESL Process (net reduction of refinery versus baselines)

<table>
<thead>
<tr>
<th></th>
<th>Water consumption</th>
<th>Arsenic trioxide emissions</th>
<th>Sulfur dioxide emissions</th>
<th>GHGs emissions</th>
<th>Unstable arsenic species to soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(m³/tonne Cu)</td>
<td>(tonnes/tonne Cu)</td>
<td>(tonnes/tonne Cu)</td>
<td>(tonnes/tonne Cu)</td>
<td>(tonnes/tonne Cu)</td>
</tr>
<tr>
<td>Baseline 1</td>
<td>Concentrate 1</td>
<td>3.18</td>
<td>0.020</td>
<td>0.15</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>Concentrate 2</td>
<td>2.28</td>
<td>0.008</td>
<td>0.10</td>
<td>1.33</td>
</tr>
<tr>
<td>Baseline 2</td>
<td>Concentrate 1</td>
<td>3.18</td>
<td>0.020</td>
<td>0.15</td>
<td>2.21</td>
</tr>
<tr>
<td></td>
<td>Concentrate 2</td>
<td>2.28</td>
<td>0.008</td>
<td>0.10</td>
<td>2.39</td>
</tr>
</tbody>
</table>

For the production of 60,000 tonnes of copper per year, using the CESL Process instead of traditional processing routes would result in decreased:
• fresh water consumption of at least 136,800 m³ per year
• particulates of arsenic trioxide to the air of at least 480 tonnes per year
• sulfur dioxide emissions of at least 6,000 tonnes per year
• greenhouse gas emissions (carbon dioxide) of at least 52,800 tonnes per year
• unstable arsenic species to ground (as arsenic trioxide) of at least 9,000 tonnes per year

Water
For areas where water is scarce and must be shared with local communities, agriculture and other industry, the use of the CESL Process for processing high-arsenic copper-gold concentrates versus the traditional treatment route would result in 20 to 23% less water consumption annually. In Peru, annual water use per person is estimated at 3 m³/day (Mekonnen & Hoekstra, 2011). For perspective, a savings of 136,800 m³/year water consumption is equivalent to the annual consumption of 45,600 people.

Air
By reducing air pollution levels, countries can reduce the burden of disease from stroke, heart disease, lung cancer, and both chronic and acute respiratory diseases, including asthma (WHO, 2016). In 2014, 92% of the world’s population was living in places where the WHO air quality guidelines were not met (WHO, 2016). A custom refinery using the CESL Process would not emit any particulates or sulfur dioxide to the air. The traditional treatment routes are estimated to emit 480 tonnes per year of particulates as arsenic trioxide and 6,000 tonnes per year of sulfur dioxide.

Climate
The use of the CESL Process in a custom refinery to treat high-arsenic copper-gold concentrates versus traditional treatment routes would result in a 27% to 57% reduction of carbon dioxide emissions, depending on the concentrate feed. In Peru, annual carbon dioxide emissions are estimated at 1.9 tonnes per person per year (World Bank, 2017). A savings of 52,800 tonnes/year carbon dioxide emissions is equivalent to the carbon dioxide emissions of 28,235 people.

Soil
A custom refinery using the CESL Process in a custom refinery for high-arsenic copper-gold concentrates versus the traditional treatment routes would result in no unstable arsenic species for ground disposal, in comparison to the estimated 9,000 tonnes per year generated by a smelter. The stability of CESL Process residues has been proven through both short and long-term stability tests.

Residue Stability
Residues from the CESL Process exhibit excellent short-term stability with 0.05 to 0.10 mg/L solubilized arsenic in leachates from the United States EPA’s Toxicity Characteristic Leaching Procedure (TCLP) tests. The stability of the residues for long-term disposal has been continuously tested under accelerated conditions for nearly four years, with arsenic dissolution well below the TCLP limit at an average of 4% of the TCLP limit of 5 mg/L arsenic in solution.
CONCLUSIONS
The environmental benefits of using the CESL Process to process high-arsenic copper-gold concentrates and produce 60,000 tonnes per year of copper metal, compared to conventional processing routes include at least:

1. 136,360 m³ of fresh water saved
2. 480 tonnes of arsenic trioxide particulates to air avoided
3. 6,000 tonnes sulfur dioxide emissions to air avoided
4. 52,800 tonnes of carbon dioxide emissions to air avoided
5. 9,000 tonnes of unstable arsenic species for ground disposal avoided

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