Reducing fresh water use in the production of metals

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ABSTRACT
Water supply plays an important role in all mining ventures, particularly with projects in water scarce regions. A comprehensive water supply strategy for mining projects is important to ensure that fair allocation of water is maintained for municipal, agricultural and industrial users in the region. The consumption of fresh water for processing copper concentrates can be substantially reduced through the adoption of hydrometallurgical processes that incorporate salt water; particularly when compared to pyrometallurgical processes that require fresh water.
Developed by Teck, the CESL hydrometallurgical process allows for the incorporation of salt water to reduce fresh water requirements in the processing of copper concentrates. Further, it should be noted that water additions to the process are already minimized through reclaiming process water by use of a closed-circuit evaporator. Bench-scale testwork is presented which demonstrates the opportunities related to salt water additions on metal recovery and overall metallurgical performance. An average copper extraction of 97.3% was achieved while fresh water consumption was decreased from 1.63 m$^3$/t concentrate to 0.67 m$^3$/t concentrate through salt water substitution. Conceptual economic benefits of salt water addition to the flowsheet are presented. Results from fully integrated pilot scale trials are discussed which show no negative metallurgical impacts of salt water integration on settling characteristics or residue stability.

Keywords: Hydrometallurgy, Copper, Salt Water, Fresh Water, Refining
INTRODUCTION

Availability of fresh water for mining projects, particularly in arid regions, is an important consideration for all stakeholders. There are several recent examples in the resource industry where resource development projects have been slowed or halted based on issues relating to water supply and management. Water use in mining/mineral concentration and concentrate processing/refining is divided among several main operating steps. Largest among these is the process to produce mineral concentrates. Water losses from this stage of the process include moisture contained within concentrate, evaporation, and water lost to tailings. There are several common methods used to reduce the amount of fresh water used in mineral concentration. These include:

- Water Control and Recycling
  - Adequate measurement and control of water inputs to the plant
  - Use of high efficiency thickeners to decrease water losses to tailings
  - Recovery of water infiltration from tailings for use in the process
  - Recycling of tailings runoff to the process
- Water Substitution
  - Use of wastewater/grey water in the process
  - Use of desalination plants for water supply
  - Direct use of sea water

Of the methods listed, water control and recycling has been employed successfully at mine sites to decrease the volume of fresh water required. For areas where availability and access to fresh water is limited, water substitution is evaluated on a case-by-case basis and often fulfills the fresh water needs of the project. Freeport-McMoran’s Cerro Verde project is constructing a wastewater treatment plant to meet site water requirements as well as those of the nearby communities [International Council on Mining and Metals (ICMM), 2012].

Two examples in Chile’s arid northern region where design considerations for reduced water consumption have been adopted are the application of desalination at BHP’s Escondida mine [Brantes & Olivares, 2008] and the direct use of sea water at Antofagasta’s Esperanza mine [ICMM, 2012]. In both of these cases, the mine/concentrator are located in an area where direct access to fresh water is limited and water (either desalinated or seawater) is pumped a significant distance from the coast to higher elevations to supply the plant. The application and effectiveness of these measures to decrease fresh water usage is case specific and varies widely based on factors such as mine location, ore body mineralogy, and impact on flotation performance. Brantes & Olivares [2008] list average concentrator fresh water usage as 0.79 m$^3$/t ore processed with a range of 0.3 – 2.1 m$^3$/t ore processed.

For processing of copper sulphide concentrates through smelting, water is required for cooling and washing of smelter gases as well as in the acid plant. Similar to concentrators, water usage can vary between operations. A report commissioned by the Chilean Copper Commission (Cochilco) in 2008 [Brantes & Olivares, 2008] lists the average fresh water consumption for a smelter as 3.6 m$^3$/t concentrate processed. Using Codelco’s Ventanas smelter as an example, a fresh water value of 3.1 m$^3$/t concentrate can be calculated based on numbers reported by the company in their 2011 sustainability report. Another source [Norgate & Lovel, 2006] quotes smelter water consumption of 7.8 m$^3$/t copper cathode for Boliden’s Rønnskar operation. Referring to Rønnskar’s more recent sustainability report from 2012, a value of 8.2 m$^3$ fresh water/t copper cathode can be calculated.

Assuming 25% copper contained in concentrate, a range of 2.0 – 3.6 m$^3$/t concentrate will be used as a benchmark to contrast the water consumption required for Teck’s CESL copper process. To
reduce the variability in the analysis to follow, focus will be placed on comparing the following two methods for refining copper concentrate: pyrometallurgical processing through a smelter-refinery, and hydrometallurgical processing by use of the CESL process. As the same fresh water consumption is assumed for the production of concentrates prior to the refining stage, the fresh water consumption in the mine and concentrator is not considered in the analysis.

**CESL CASE**

Teck has developed a hydrometallurgical process, called the CESL process, as an alternative to conventional smelting and refining of copper concentrates for the production of LME Grade A copper cathode [Bruce et al., 2011]. The CESL copper process is a medium temperature pressure leach for sulphide concentrates in the presence of chloride catalytic ions (12 g/L). Based on the presence of chloride in the process, materials of construction for a CESL refinery are specified for a corrosive environment, which uniquely positions the process for the incorporation of chloride bearing salt water into the flowsheet. This includes salt water or, potentially, hypersaline bore water prevalent in some desert regions. This section outlines testwork that has been carried out to investigate the impact of salt water on metal recovery and the overall metallurgical performance of the process.

**Bench testwork**

Bench testwork was recently conducted on a copper sulphide concentrate containing chalcopyrite and bornite. To determine the appropriate test conditions, specifically the concentration of dissolved salts in the recycled process solution, a METSIM model was constructed. Figure 1 presents a block diagram of the flowsheet used for modeling that highlights main water inputs to the process.

In Pressure Oxidation (PO), concentrate is reground and then fed to an autoclave along with recycled acid feed liquor. Oxygen is injected into the autoclave at 150°C and 1380 kPag to oxidize and leach the minerals. Depending on the degree of acid production in the autoclave, any remaining oxidized minerals are leached from the PO solids at atmospheric conditions. Acid required for Atmospheric Leach (AL) is provided from recycled, acidic raffinate generated in Solvent Extraction (SX). Following AL the residue is washed in Counter Current Decantation (CCD) with process water to retain soluble metals and chloride. Pregnant leach solution (PLS), consisting of overflow streams from the PO thickener, AL thickener, and first CCD thickener, is sent to SX for copper recovery using standard SX/EW technology. Acidic raffinate is sent to an Evaporator circuit where water is removed to control the plant water balance. Condensate produced in the Evaporator circuit is used as process water in the plant creating a closed water balance with no liquid effluents. Finally, a portion of the Evaporator product is processed through a low pH (1.8) Neutralization circuit for excess sulphate removal.
Fresh water consumption and supply for the base case model (no salt water incorporation) are shown in Table 1. Fresh water inputs were considered for substitution, in part, with salt water.

**Table 1** Water supply and consumption distribution for the base case model

<table>
<thead>
<tr>
<th>Water supply</th>
<th>m³/t conc.</th>
<th>Distribution</th>
<th>Water use</th>
<th>m³/t conc.</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh water</td>
<td>1.63</td>
<td>51%</td>
<td>Residue Wash</td>
<td>2.19</td>
<td>68%</td>
</tr>
<tr>
<td>Evaporator condensate</td>
<td>1.56</td>
<td>49%</td>
<td>Grinding</td>
<td>0.53</td>
<td>17%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Reagent Makeup</td>
<td>0.28</td>
<td>9%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Electrowinning</td>
<td>0.19</td>
<td>6%</td>
</tr>
</tbody>
</table>

Water addition to Electrowinning (EW) requires low levels of impurities in the interest of product quality as well as to protect the cathode blanks from chloride corrosion, making saline water unsuitable for this application. It is also assumed that concentrate repulping is carried out in fresh water. Salt water substitution was examined for all other water requirements which make up 77% of the total water consumption in the plant. Water required for sealing of pumps as well as gland water to the autoclave agitators was not considered.

Typical salt water composition used for modelling purposes is presented in Table 2. Taken from an online source [Lenntech, 2014] these values were used to determine the solution composition for bench testwork.
Table 2 Salt water composition

<table>
<thead>
<tr>
<th>Element</th>
<th>Chloride (Cl(^-))</th>
<th>Sodium (Na(^+))</th>
<th>Sulfate (SO(_4^{2-}))</th>
<th>Magnesium (Mg(^{2+}))</th>
<th>Calcium (Ca(^{2+}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (g/L)</td>
<td>18.7</td>
<td>10.4</td>
<td>2.5</td>
<td>1.3</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Several scenarios were run with increasing salt water content from 4%-30% of the total water requirement for the plant. Acid feed concentration targets were taken from each of these scenarios and a series of bench-scale leach tests were conducted in a 2L, titanium cast Parr autoclave. Operating conditions for the tests are presented in Table 3. Each pressure oxidation test was followed by an Atmospheric Leach conducted at a pH of 1.5-1.8 for 2 hours to complete the copper leaching.

Table 3 Bench test leach operating parameters

<table>
<thead>
<tr>
<th>Condition</th>
<th>Unit</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids density</td>
<td>g/L</td>
<td>200-210</td>
</tr>
<tr>
<td>Pressure</td>
<td>kPa</td>
<td>1380</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>150</td>
</tr>
<tr>
<td>Retention time</td>
<td>min</td>
<td>60</td>
</tr>
<tr>
<td>Acid feed [FA]</td>
<td>g/L</td>
<td>60</td>
</tr>
<tr>
<td>Acid feed [Cl(^-)]</td>
<td>g/L</td>
<td>11-24</td>
</tr>
<tr>
<td>Acid feed [Na(^+)]</td>
<td>g/L</td>
<td>0-6</td>
</tr>
<tr>
<td>Acid feed [Mg(^{2+})]</td>
<td>g/L</td>
<td>0-2.8</td>
</tr>
</tbody>
</table>

Bench metallurgical results

Outcomes of greatest interest in this series of tests were the potential impact of salt concentration on metal extraction and sulfur oxidation, which have the greatest economic impact on the process. Finally the precipitation of sodium, one of the main impurities present in salt water, is considered.

Metal Extraction

Copper extraction in the CESL process for a copper sulfide concentrate containing chalcopyrite and bornite has been demonstrated to exceed 97% [Bruce et al., 2011]. Figure 2 presents the copper extraction achieved at varying levels of salt water substitution for fresh water. Copper extraction for all tests averaged 97.3%. All results fell within 2 standard deviations of this mean value.
Sulfur Oxidation

Sulfur oxidation within the CESL process has been demonstrated to be limited to a fraction of the sulfur present in the concentrate. This limits operating costs associated with oxygen consumption as well as limestone for neutralization of acidic process streams. Higher sulfur oxidation increases the amount of gypsum residue produced, resulting in increased water consumption for washing of solids.

Sulfur oxidation is closely related to percent pyrite contained in a concentrate but can be impacted by other factors such as chloride and sulfate concentrations. Figure 3 presents the sulfur oxidation measured in the bench tests. A small increase (5% absolute) in sulfur oxidation was noted with increasing salt concentration in the autoclave feed solution.

Sodium Precipitation

Sodium is one of the impurities present in salt water that does not have a convenient method of removal (i.e. neutralization) from the CESL flowsheet. A certain portion of the sodium fed to the autoclave precipitates as natrojarosite by reaction (1).
$Na_2SO_4 + 3Fe_2(SO_4)_3 + 12H_2O \rightarrow 2NaFe_3(SO_4)_2(OH)_6 + 6H_2SO_4$  \hspace{1cm} (1)

From the bench results the percentage of sodium precipitation decreases with salt concentration in the acid feed. This trend continues until sodium precipitation reaches a value of 20%, at which point the trend stabilizes. This is an important factor to consider for flowsheet design as precipitation of sodium in the autoclave, along with minor solution entrainment in the final residue, are the only mechanisms for sodium removal in the CESL flowsheet as it is a closed water balance.

**Water usage**

As the amount of salt water added to the flowsheet increases, there is a direct reduction in fresh water consumption. At 30% salt water substitution fresh water additions are only required for Electrowinning make-up solution and concentrate repulping in Grinding. Figure 4 presents a comparison of the fresh water consumption for smelting and that required for the CESL process. Fresh water consumption for the CESL base is 18 – 55% lower than that of the smelting case. With 30% salt water substitution, the fresh water consumption for the CESL flowsheet is 66 – 80% lower than that of the smelting case. On an intensity of use basis smelting uses 3x to 5x more fresh water than a modified CESL hydrometallurgical process (30% salt water substitution for fresh water).

![Figure 4](image)

**Economic impact**

Economic impact of salt water incorporation to the CESL flowsheet was examined on the basis of: (i) decreased HCl additions to maintain chloride concentration in the plant inventory, and (ii) the decreased cost related to reduced requirements for fresh water. Capital cost was not considered on the basis of the CESL process already requiring moderate (12 g/L) levels of chloride in the process inventory. Titanium would be specified in most applications, though recent work has shown that application of super duplex steels in certain low temperature applications may be possible [Riha, Bruce & Schwartz, 2013]. Table 4 presents the operating cost savings resulting from salt water addition for a project where use of desalination is required.
Table 4 Operating cost savings of salt water addition when desalination is required

<table>
<thead>
<tr>
<th>Salt Water Addition</th>
<th>Unit</th>
<th>0%</th>
<th>4%</th>
<th>8%</th>
<th>12%</th>
<th>15%</th>
<th>23%</th>
<th>31%</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl addition</td>
<td>kg/t conc.</td>
<td>6</td>
<td>0.76</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fresh water addition</td>
<td>m³/t conc.</td>
<td>1.63</td>
<td>1.58</td>
<td>1.44</td>
<td>1.33</td>
<td>1.26</td>
<td>0.81</td>
<td>0.67</td>
</tr>
<tr>
<td>HCl cost savings</td>
<td>C/lb Cu</td>
<td>0</td>
<td>0.27</td>
<td>0.31</td>
<td>0.31</td>
<td>0.31</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>Fresh water savings</td>
<td>C/lb Cu</td>
<td>0</td>
<td>0.06</td>
<td>0.16</td>
<td>0.25</td>
<td>0.32</td>
<td>0.61</td>
<td>0.74</td>
</tr>
<tr>
<td>Total savings</td>
<td>C/lb Cu</td>
<td>0</td>
<td>0.33</td>
<td>0.47</td>
<td>0.56</td>
<td>0.62</td>
<td>0.92</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Unit costs used for HCl and desalinated water in this analysis are: US$280/t HCl (@34%) [vendor quote] and US$2.8/m³ of desalinated water [Soruco & Philippe, 2012]. Based on this data the cost savings for salt water addition were 0.33 – 1.05 cents/lb Cu cathode.

An internal tradeoff study conducted by Teck determined the costs for delivery of water to a site located at an elevation of 2000 m above sea level to be $1.4/m³ for sea water. One source [Soruco & Philippe, 2012] gives the operating cost of delivery for desalinated water as $2.8/m³. Using these values three cost scenarios were considered for salt water substitution: a project where abundant fresh water was available ($0.2/m³ fresh water), one where fresh water availability was limited ($1.0/m³ fresh water), and one using desalinated water ($2.8/m³ desalinated water). Figure 5 presents CESL process annual savings associated with 30% salt water substitution for each water constraint scenario, based on 100,000 tpy copper production, compared to the CESL base case where no salt water is used.

![Figure 5 Yearly savings using salt water in the CESL process](image)

In the case where abundant fresh water is available the introduction of salt water results in yearly savings of $276,000. This is mainly attributed to the decreased requirement for HCl addition to maintain chloride concentrations in the plant. For the case where fresh water supply is limited the use of sea water would result in yearly savings of $900,000. For the case where desalinated water is being used savings of using salt water amount to $2.3 million annually. This data only considers the operating cost of producing desalinated water and conveying it to the project site; capital cost was
not considered. All three cases present an opportunity for cost savings. However, in cases where fresh water is unavailable or where restrictions prevent its use, the use of salt water provides a significant economic benefit when compared to the cost of desalinated water.

**Pilot plant trial**

Previous pilot plant testwork has been conducted, on a different, although mineralogically similar, copper sulphide concentrate than that used for the bench testwork, which examined salt water addition to the CESL flowsheet. As part of a client project a two week pilot plant trial was conducted. For the case tested, integration of the CESL refinery with an existing heap leach was considered as an attractive option. Figure 6 presents a diagram of the flowsheet considered.

![Heap leach integration flowsheet](image)

Heap leach integration allowed for the elimination of several unit operations based on the ability of the heap leach to utilize acid produced through sulfur oxidation, negating the requirement for a neutralization circuit. Based on the presumed evaporation expected within the heap leach operations, the Evaporator circuit was also eliminated from the flowsheet. Salt water addition was used to provide a large portion of the autoclave feed liquor (32%) as well as a portion of the wash solution for the leach residue (25%).

Table 5 presents leach circuit metallurgical results for the pilot trial where the plant was operated with and without the use of salt water. Similar to the bench testwork presented, copper extraction was not impacted by salt water addition to the flowsheet. A slight increase in sulfur oxidation was observed.

**Table 5** Leach circuit metallurgical results for pilot trial

<table>
<thead>
<tr>
<th>Operating results</th>
<th>Units</th>
<th>Fresh water</th>
<th>Salt water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper extraction</td>
<td>%</td>
<td>97</td>
<td>97</td>
</tr>
<tr>
<td>Sulphur oxidation</td>
<td>%</td>
<td>33</td>
<td>34</td>
</tr>
</tbody>
</table>
In addition to the variables presented in Table 5, performance of the integrated flowsheet was also consistent for both cases. This included residue settling characteristics, residue stability, and SX performance. Residues produced while incorporating salt water were washed in a thickener train. Thick underflow densities, in excess of 50% solids, were maintained throughout the salt water trial. Standard USEPA Toxicity Characteristic Leaching Procedure tests (TCLP) were conducted on the washed residues produced. Samples of residues produced without salt water addition were tested as well as those produced with salt water added to the flowsheet. Both samples met the USEPA standard for all elements and no significant increase in leachable metals was detected for the sample produced using salt water. Finally, solvent extraction performed well with no additional transfer of impurity elements to the electrolyte, allowing for the production of LME Grade A copper cathode.

CONCLUSION
As compared to the fresh water consumption rate of 2.0 - 3.6 m$^3$/t concentrate for pyrometallurgical smelting and refining of copper, the CESL base case provides an opportunity to decrease water consumption by 20 - 50%, at 1.63 m$^3$/t concentrate. The use of salt water decreases fresh water consumption to less than 1.0 m$^3$/t conc., a decrease of 66-80% when compared to smelting.

Substitution of fresh water with salt water in the CESL process provides an economic benefit in all cases but this benefit is most pronounced for projects where an alternative to fresh water use is required, such as desalination. Another added benefit of using salt water is the ability to process directly concentrates from milling and concentrator operations that have adopted salt water processing, while also capitalizing on the learnings and operating practices of these mills.

Water supply for mining and metal refining is a topic that has seen much attention over the last decade and this trend is likely to continue. To meet increasing global demand for copper while ensuring adequate water availability for all stakeholders, the copper industry needs to focus on decreasing the requirements for fresh water and increasing efficiency in its use in all aspects of the mineral and metal production process.

REFERENCES


