ABSTRACT

Mining operations are often a very intensive water user. Improving water efficiency is a critical objective of the industry to keep operations sustainable while reducing the environmental impact. El Teniente site, a copper mine located in Chile is currently equipped with a cobalt removal water treatment plant before discharge to the environment. Some extensive pilot tests were conducted using softening, ultrafiltration and reverse osmosis for further reducing the effluent sulphate concentration. The results show stable operation of the two-stage membrane process with and without pre-softening. Additional tests on the reverse osmosis brine were successfully conducted to post-precipitation the super-saturated gypsum and further reduce the concentration of sulphate.

INTRODUCTION

Mining operations are often a very intensive water user. Improving water efficiency is a critical objective of the industry to keep operations sustainable while reducing the environmental impact. Water management in mines has its specific challenges, related to the nature of the water, the source of pollutant and the location, which is usually remote with limited access to resources and waterways. The “pollution” can come from the mining process itself, or from the water quality extracted as part of the mining activity. Water treatment objectives are driven by the process characteristics in the case of recycling, or by the water body the water is discharged in and associated environmental regulations. Location appears indeed a critical point as water scarcity increases interaction between users. This concerns all mining activities from coal to metal ore.

In this context, innovative water solutions to reduce the mining water footprint are a critical factor for development and competitiveness. The range of treatment processes includes mainly clarification – coagulation/adsorption and separation – and more recently salt removal using softening and membrane technologies. The selection and integration of different processes and technologies allow the optimisation of the treatment line. Cost effective, reliable and easily operability solutions are key for the mining application, especially when the mine is in a remote location.

The aim of this presentation is to focus on one case study, illustrating the processes and technologies used on a Chilean mine to manage Acid Mine Drainage, reduce the environmental impact and in an effort to extend to increase water recycling possibilities.

CONTEXT

Chile is the 38th largest country in the world. The country has abundant metals and minerals, especially in its northern desert region. None of these is more important than copper, for which Chile is widely known as the world’s number one producer. Reserves of fine copper are estimated to be in excess of 100 million tons. In 2012, Chile was the world’s leading producer of copper, accounting for 32% of world mine production (Anderson, 2014).

Copper has made mining a key sector of Chile’s economy, although the country is also the producer of gold and molybdenum, secondary products of copper extraction. According to Chilean Copper Commission (Cochilco), the country’s copper production would exceed 6 million tons by 2015 and 8 million tons by 2025. Codelco: The state-owned Chilean group is the world’s single biggest copper producer, controlling about 20 percent of total global reserves (Goro, 2012). The company produced about 1.76 million metric tons of copper in 2010.

Two main processes can be used to extract copper:

1- solution exchange electrowinning (SX-EW): the ore (copper sulphate) is first broken and set out on leach pads where it is dissolved by a sulphuric acid solution to leach out the copper. The copper-rich solution is then pumped to the solvent extraction plant to separate the copper as a copper complex. This is concentrated and the solution is passed to the electrowinning plant to recover the copper. The copper cathodes produced by electrowinning contain 99.99% copper which is suitable for electrical uses.

2- Extraction – Concentration - The traditional method used at most mines involves the ore (copper oxid) being broken and brought to the surface for crushing. The ore is then ground finely
before the copper-bearing sulphide minerals are concentrated by a flotation process which separates the grains of ore mineral from the waste material, or gangue. The concentrate is then processed in a smelter and electrolytically refined. This second method is mainly used at El Teniente.

Codelco, El Teniente (“The Lieutenant”) division, is the largest underground copper deposit in the world. El Teniente is an underground copper mine located in the Chilean commune of Machalí in Cachapoal Province, the O'Higgins Region, 2,300m above mean sea level in the Andes (Figure 1). The mine has currently more than 3,000 kilometers of galleries. El Teniente Mine has an ore extraction capacity of 150,000 tonnes / day for an output rate of approximately 450,390 tpy of fine copper (Codelco, 2013) and a capacity of 6,500,000 tpy of Molybdenum (Anderson, 2014). Tailings from the mine are transported through a 90 km channel to the Carén impoundment. This intermediate water body has a 22 km² surface, a 725,000,000 m³ storage and offers an average of 10 years buffer capacity. The water pH is neutralised up-stream entering the Carén impoundment allowing precipitation to occur: Gypsum and metals settle naturally. The Caren impoundment discharges at variable flow rate to a natural sensitive wetland used for irrigation and livestock drinking water supply (Figure 2).

The mine discharge Standards are expected to get more stringent on sulphate in the near future. In this context, Degremont with its client Sodelco and its partner DOW chemical, conducted some pilot tests to evaluate additional processes to reduce the sulphate discharge.

EXISTING EFFLUENT TREATMENT FACILITY

To achieve the current discharge limits, the effluent from the Carén impoundment is treated through a 2.5 m³/s Molybdenum Removal Plant (Figure 3). The Plant has been designed and built by Degremont in 2005, and has been successfully operated by Degremont since then. The main treatment is performed using a proprietary process based on coagulation and contact flocculation and combined clarification and thickening. The plant molybdenum removal rate is set in accordance with the inlet molybdenum concentration (Table 2).

Table 2: PAMo molybdenum target objectives

<table>
<thead>
<tr>
<th>Mo inlet (mg/L)</th>
<th>&lt;1.5</th>
<th>1.5-2.5</th>
<th>2.5-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal rate (%)</td>
<td>70</td>
<td>80</td>
<td>90</td>
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Since 2005, PAMo plant has been operated by Degremont operation teams under a 5-year O&M contract. The operation personnel operate the plant, conduct water quality analysis, perform the maintenance of the equipment and assist in technical support.

PAMo site has been used to house a pilot test for the demonstration of further sulphate removal process.

TECHNOLOGIES AND PROCESSES
Several processes can be used for the removal of sulphate (LORAX, 2003), including:

- Chemical treatment (Limstone/lime and precipitation of gypsum; Baryim sulphate precipitation; ettringite precipitation)
- Membrane treatment; reverse osmosis (water or slurry precipitation); Electrodyalisis reversal;
- Ion exchange;
- Biological sulphate removal.

The chemical treatments (precipitation) are usually recognised as the most cost effective, but generate a huge quantity of sludge.

Membrane process is more sensitive to feed water quality and exposed to scaling. Nevertheless, it presents the advantage of low chemicals consumption, and low sludge production compared to the chemical treatments. Indeed low chemicals consumption can be a real advantage for remotely located plant, due the the difficult access and transportation cost. The sludge production is also a key as it needs to be stored and can generate additional environmental impact to be taken into consideration in the whole project evaluation.

The membrane process has been selected for this study to further optimise the pre-treatment, monitor and assess the desalting performances and scaling, and propose a solution for the brine treatment.

MATERIAL AND METHODS
The demonstration unit includes a large scale pilot plant based on sulphate removal process using a high rate contact clarifier (40 m³/h capacity) for pre-softening, a clarification polishing step performed on dual media filters and ultrafiltration (polysulfone membrane), and a salt removal treatment using a 2-stage salt removal membrane process (Figure 4). The salt removal skid includes 4” elements, 6 membrane per pressure vessel in a 2/1 configuration. The unit has been operated at 70% conversion rate.

The main objectives of the pilot test were:
- To assess the use of pre-softening on the PAMo effluent, and subsequent impact on the filtration and reverse osmosis performances;
- To evaluate both media and ultrafiltration filtration processes in terms of fouling rate, cleaning and filtered water quality for the feed of reverse osmosis process;
- To test salt removal process on a long term basis, to assess both sulphate removal performances and scaling control through antiscalant dosing;
- To evaluate brine post treatment including over-saturated precipitation before disposal.

The study has been conducted over one year at the Molybdenum Removal Plant to evaluate both processes performances and long term operation.

The team focussed mainly on the softening process and the management of scaling potential on the nanofiltration membrane.

RESULTS AND DISCUSSION
The water quality characteristics measured during the one-year pilot test is summarised in table 3. The conductivity of the PAMo plant treated water range 2,800 to 3,500 microS/cm. The water is mainly composed of sulphate and hardness, the sodium and chloride representing less than 10% of the total dissolved solids. Aluminium, iron and manganese are present, as well as remaining trace of molybdenum.
The pilot has been operated over one year, from end of 2013 to end of 2014.

### Table 3: Water quality feeding the pilot plant

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Min.</th>
<th>Max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride / Sodium</td>
<td>mg/L</td>
<td>60/140</td>
<td>120/160</td>
</tr>
<tr>
<td>Al, Fe, Mn</td>
<td>mg/L</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Hardness (Ca, Mg)</td>
<td>mg/L</td>
<td>500</td>
<td>800</td>
</tr>
<tr>
<td>Sulphate</td>
<td>mg/L</td>
<td>1,500</td>
<td>2,000</td>
</tr>
<tr>
<td>Conductivity</td>
<td>microS/cm</td>
<td>2,800</td>
<td>3,500</td>
</tr>
</tbody>
</table>

### Pre-softening

Pre-softening objectives are to remove part of the calcium and reduce the risk of gypsum precipitation on the following filtration and reverse osmosis membranes. Indeed, Gypsum represents a risk of scaling on the reverse osmosis treatment. The unit operated with soda ash ($\text{Na}_2\text{CO}_3$), ferric chloride for the coagulation and flocculant aid (organic polymer) to assist in the clarification process.

The pre-softening process operated according to 3 regimes: partial softening, total softening and unit by-passed with a direct feed of the RO pre-treatment filtration from the PAMo treated effluent.

The main interest of the pre-softening process appears to be the polishing effect on the residual metals (Fe, Mn). Indeed, with the unit totally by-passed, the reverse osmosis unit operated in a steady condition over several months without major scaling problem. The sludge produced during the softening treatment appears very dense and already thickened thanks to the Densadeg contactor process.

### Clarification polishing treatment

The pilot plant included a first stage of media filtration, followed by an ultrafiltration stage. The main objective of the filtration was to pre-treat the water and remove particles before feeding the reverse osmosis membrane. The ultrafiltration used was a skid mounted unit equipped with polysulfone in-out membrane operated in dead end mode. Filtration cycles were 1.5 hours.

The filtration stage run in steady operation without major ultrafiltration membrane fouling. Ultrafiltration membrane cleaning was performed every 100 days through the period of test. The cleaning chemical used was citric acid (pH 4) to remove any scaling and metal precipitates. The filtered water quality had a SDI consistently below 2 %/min.

### Salt removal membrane treatment

Salt removal treatment was evaluated over one year in steady process operating conditions, but with variable feed water quality as the softening process operation was adjusted. The membrane filtration flux was increased from 17.9 to 19 L/h/m$^2$ after several months of operation without noticeable impact on the membrane permeability. During the increase of the calcium concentration at the membrane feed (softening treatment reduced and by-passed) the super saturation level in the brine was carefully monitored (Figure 7), and the antiscalant dosing rate was adjusted accordingly to avoid scaling as expected. The overall treatment achieved the expectations in terms of fouling and salts rejection.

### Brine treatment

To complete the pilot study, some tests were performed on the brine produced by the last salt removal stage, to identify the best condition to de-saturate the gypsum and reduce the accumulated concentration of sulphate. The study was conducted in the lab, using Jar Test to evaluate different conditions of pH and chemicals dosing regimes. The kinetic of precipitation was an important parameter to characterise, as the brine was stabilised by the use of antiscalant. The best conditions of post precipitation were determined using an additional dosing of ferric sulphate to assist in the clarification of the gypsum naturally formed (Figure 8).

CONCLUSION
Acid mine drainage, the outflow of acidic water from metal mines or coal mines generate effluents containing high metals residual from the mining activity as well as high concentration of sulphate. The discharge of those effluents to the environment or the reuse of this water in further process is a challenge faced by most of the mines around the Globe.

The case study of the copper mine El Teniente, and the pilot test conducted on the site of PAMo illustrate the challenge, the difficulties and presents a technical solution, combining technologies, including conventional and advanced membrane applications. The main difficulties faced included the selection of the optimum pre-treatment and degree of hardness removal, the selection of the appropriate anti-scalant and dosing, and the related salt removal scaling risk management. The experience gained in Chile can be easily applied to Australian mine sites.

ACKNOWLEDGMENT

This authors would like to thanks Codelco and DOW, as well as the PAMo operation team for their assistance in conducting this study.

REFERENCES


Figure 2: El Teniente, copper mine located in the Chilean commune of Machalí in Cachapoal Province, the O’Higgins Region – View of the Caren impoundment

Figure 3: Molybdenum removal plant, treating the El Caren Tailing impoundment water
Figure 5: View of the pilot plant