Improvements in RO Technology for Difficult Feed Waters

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ABSTRACT
Water for sustainable mining operations is a precious and limited resource, especially in arid areas of Chile. The Chilean copper mining industry requires a large amount of highly purified water for every pound of copper produced. Frequently the feed waters that need to be purified are impaired and can be difficult to treat due to high fouling rates which can adversely impact the ability to produce the quality and quantity required on a continuous 24/7 basis. RO (reverse osmosis) is an excellent technology for purifying water in that it can remove TDS (total dissolved salts) and TOC (total organic carbon), but its operation can be difficult if the rate of fouling is excessive. Fouling can be controlled by a well designed pretreatment system to remove foulants, by a well designed RO system, and by a well trained operating staff.

LD Technology™ is a RO feed spacer and membrane technology that has been developed for use in spiral-wound elements for the primary purpose of treating difficult waters. The element has a new, thicker 34-mil feed spacer which reduces RO feed pump energy requirements by reducing the feed-to-concentrate pressure drop, bio-static properties that reduces the rate of biological fouling, an innovative spacer geometry designed to reduce the rate of colloidal fouling and improve the effectiveness of chemical cleanings. The membrane has been improved to have higher rejection and better chemical stability to allow more aggressive cleanings.

CPA5-LD™ is a new brackish water RO membrane that has been developed to produce the best permeate quality available, with the exception of seawater RO elements. It offers the highest rejection of silica, nitrate, TDS and TOC presently available. It utilizes LD Technology and is a more robust membrane than past polyamide membranes during service operation and cleaning.

A case study will be presented indicating the effectiveness of these new technologies. Fouling has not always been completely stopped, but the rate of fouling has been reduced to allow the operations group a RO system whose operation is manageable and cleanings are less frequent and can be planned. This case study is the operation of CPA5-LD RO elements in a pulp & paper plant in Brazil which has historically struggled with a high fouling surface source.

REDUCING FOULING RATES WITH DIFFICULT WATERS
Surface waters, municipal waste waters, industrial waste and run-off waters, and some well waters are considered to be “difficult waters”. Difficult waters require additional pretreatment and a more complex design prior to the RO to remove or control a multitude of foulants. It is important to properly characterize and identify the potential foulants in the design phase, with special
consideration for changes in feed water quality due to variations in seasons, industrial operations, or man-made introduction of chemicals. Table 1 below is a partial list of suggested RO feed water guidelines to be met by pretreatment on difficult waters.

**Table 1: Suggested RO Feed Water Parameters on Difficult Waters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Design Limit</th>
<th>Design Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional Pretreatment</td>
<td>MF or UF</td>
</tr>
<tr>
<td>SDI @ 15 minutes</td>
<td>&lt; 4 (prefer &lt; 3)</td>
<td>&lt; 2.5 SDI</td>
</tr>
<tr>
<td>Turbidity</td>
<td>&lt; 0.3 NTU (prefer &lt; 0.1)</td>
<td>&lt; 0.1 NTU</td>
</tr>
<tr>
<td>Particle Counts @ 2 micron</td>
<td>&lt; 100 counts per ml</td>
<td>&lt; 20 count per ml</td>
</tr>
<tr>
<td>TOC (will be site specific)</td>
<td>&lt; 3 mg/l as C</td>
<td>&lt; 2 mg/l as C</td>
</tr>
<tr>
<td>Iron (w/o dispersant)</td>
<td>&lt; 0.3 mg/l</td>
<td>&lt; 0.3 mg/l</td>
</tr>
<tr>
<td>Aluminum (w/o dispersant)</td>
<td>&lt; 0.1 mg/l</td>
<td>&lt; 0.1 mg/l</td>
</tr>
<tr>
<td>Silica in Conc (with dispersant)</td>
<td>&lt; 230 mg/l as silica</td>
<td>&lt; 230 mg/l as silica</td>
</tr>
</tbody>
</table>

The RO system designer is faced with the challenge of balancing capital costs with operating costs. The goal is to optimize the RO operation to continuously produce the specified quality and quantity of RO permeate with minimal and predictable cleaning frequency. Table 1 above highlights that in most cases conventional pretreatment designs may be less expensive to purchase but the quality they produce in terms of colloidal fouling protection is not as good as the quality of a MF (microfiltration) or UF (ultrafiltration) system. Colloidal fouling is one of the major foulants of concern for an RO and is typically monitored by SDI, turbidity and particle count readings. Table 2 highlights the differences in RO design guidelines for conventional and MF/UF pretreatment which can have major impacts on RO system flux and number of elements and pressure vessels. Waste waters typically are more difficult to treat than surface waters, and therefore have more conservative guidelines. Given the effort and expense required to design a good RO system, it would be prudent for the selection of a RO element and membrane that aids in the reduction of fouling and frequency of cleaning. Some rule of thumbs in designing an RO system for reduced fouling are:

- Design the best pretreatment to control colloidal fouling
- Design with the lowest system average flux
- Design with the lowest lead element flux
- Design with the best flux balance between stages
• Design with the lowest delta P for each stage
• Design for highest cross-flow and concentrate flow velocities
• Design to control biological fouling
• Design with no dead-legs that breed biological foulants
• Design so you can sanitize all equipment
• Design so that the portions of the system are not stagnant for long time periods (2-8 hours)
• Design good CIP (clean-in-place) systems for the operators with VFD driven pumps
• Select the best RO membrane to handle colloidal and biological foulants

Table 2: Suggested Large RO System Design Guidelines for Difficult Waters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Surface Conventional</th>
<th>Surface MF/UF</th>
<th>Waste Conventional</th>
<th>Waste MF/UF</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Average Flux</td>
<td>17-20 lmh</td>
<td>24-27 lmh</td>
<td>12-14 lmh</td>
<td>15-19 lmh</td>
</tr>
<tr>
<td>Lead Element Flux</td>
<td>25-31 lmh</td>
<td>31-36 lmh</td>
<td>17-22 lmh</td>
<td>20-27 lmh</td>
</tr>
<tr>
<td>% Flux Decline Annual</td>
<td>7-10%</td>
<td>7-10%</td>
<td>15-18%</td>
<td>12-15%</td>
</tr>
<tr>
<td>% Salt Passage Annual</td>
<td>10-15%</td>
<td>10-15%</td>
<td>10-15%</td>
<td>10-15%</td>
</tr>
<tr>
<td>Minimum Conc per PV</td>
<td>2.7-3.6 m³/hr</td>
<td>2.7-3.2 m³/hr</td>
<td>2.7-4.1 m³/hr</td>
<td>2.7-4.1 m³/hr</td>
</tr>
</tbody>
</table>

REDUCED FOULING RATE WITH A NEW RO FEED SPACER

LD Technology™ utilizes a RO feed/brine spacer engineered to improve RO system performance for difficult waters by reducing the rate of fouling due to colloidal material and biological matter, lowering the energy cost to produce water by lowering the feed-to-concentrate pressure drop, reducing operating cost by extending membrane life, and reducing labor and chemical cost by reducing the frequency of chemical cleanings.

The LD Technology uses a 34-mil thick feed spacer while still maintaining 400 sq.ft. of active membrane area in an 8-inch diameter by 40” long RO element. Historically a 400 sq. ft. element would require a thinner 26- or 28-mil feed spacer but due to improvements in material and manufacturing techniques, which include the use of factory robotics for the accurate placement of glue lines, has resulted in the development of a 400 sq. ft. membrane with a 34-mil feed spacer. Photograph # 1 below shows the 34-mil LD membrane sitting on a membrane. The primary functions of the feed spacer is to separate the opposing membrane leaves of a spiral wound element so feed/concentrate water can freely flow between the membrane leaves while promoting a shearing form of turbulence to minimize concentration polarization at the membrane surface by enhancing the back diffusion of salts and foulants from the membrane surface.
The thicker LD feed spacer results in a number of service operating advantages due to the lower feed-to-concentrate differential pressures for each element:

- Pressure drop can be reduced up to 45% with a 34-mil LD feed spacer when compared to conventional 400 sq. ft. elements with 26-28 mil feed spacers at typical large system recoveries and fluxes. Chart 1 indicates the significant improvement in pressure drop for each element in a typical 2-stage system with six elements per stage at 80% recovery, 27.5C, 200 ppm feed TDS, and 26 l/m/h system flux.
- The unique LD geometry design also results in up to a 10% lower pressure drop than conventional 34-mil feed spacers.
- Feed pressures due to lower pressure drops can be reduced as much as 1.2 to 1.7 bar (17-24 psi) at typical large system recoveries and fluxes. This reduces energy cost.
- 1st stage lead element fluxes can be reduced up to 10% reducing the rate of fouling by colloidal material as evidenced in Chart 1 which indicates the average flux for each element in a typical 2-stage.
- Flux balance between stages can be improved up to 10% which distribute foulants more evenly over a greater area of membrane that results in reduced deposition of foulants over time.
- The thicker spacer reduces colloidal fouling by allowing particulates to move more freely through the feed path and eventually out to drain.
The thicker feed spacer, coupled with a unique geometry to the feed spacer which traps less colloidal material, results in a number of cleaning advantages over thinner feed spacers for colloidal foulants as evidenced by the increase in differential pressures in Graph 1 below. A 9-month trial on a city water source with a relatively high SDI of 4-5 shows 34-mil LD required no cleanings, one cleaning for a 31-mil spacer element and five cleanings for a 28-mil spacer element.

Chart 2: Colloidal Fouling CIP cleaning frequency for various size feed spacers
The LD Technology has also been engineered to reduce the rate of biological fouling. The feed spacer material has been chemically enhanced with a biostatic compound. The biostatic properties reduces the impingement of biological matter (e.g. bacterial, algae, fungi) onto the feed spacer and creates a biostatic zone around the spacer which stretches to the membrane surface, as highlighted by Photograph 2. Photograph 3 shows the reduced fouling of a LD biostatic feed spacer versus a conventional RO element’s feed spacer.

**Photograph 2: Biological fouling with LD biostatic feed spacer versus conventional spacer**

![Photograph 2: Biological fouling with LD biostatic feed spacer versus conventional spacer](image)

**Photograph 3: Biological fouling of conventional feed spacer versus LD biostatic feed spacer**

![Photograph 3: Biological fouling of conventional feed spacer versus LD biostatic feed spacer](image)

**HIGHEST REJECTING BRACKISH WATER RO ELEMENT**

The LD feed spacer technology can be used with any NF or RO membrane spiral wound device. The CPA5-LD polyamide-based RO membrane is the newest generation of high-rejecting brackish water RO membranes and is rated at 10,000 gpd at 225 psi. At 99.7% nominal salt rejection, it has improved rejection for organic matter and for inorganics when compared to the past 99.5%
rejection membranes. Chart 3 indicates the improved rejection of organics, especially at the lower molecular weights, with a reduction in organic passage in some cases over 50%. Actual TOC rejection will vary and will be site specific but it will typically be better than the earlier membranes. Chart 4 indicates the improvement in individual inorganic ions, particularly for silica and nitrate. This membrane is also robust, as evidenced by the wide CIP cleaning range of 1-12 pH, which makes it suitable for use with difficult water sources which will require more frequent cleanings than better pretreated feed water systems.

**Chart 3: CPA5 enhanced rejection of organics**

**Chart 4: CPA5 enhanced rejection of inorganics**
CASE STUDY: PULP & PAPER MILL RO SYSTEM IN BRAZIL

A large pulp & paper mill in Brazil has been operating for years a RO system on high fouling surface water. They have had a history of frequent cleaning due to a combination of colloidal fouling, organic fouling, and biological fouling. There are seven RO trains using a number of membrane suppliers, with each train being a 16x8-6M array rated at 115m3/hr and 75% recovery. The pretreatment is conventional and includes coagulation with chlorination, alum, sand filters, multimedia filters, cartridge filters, sodium bisulfite for dechlorination, and antiscalant for the control of barium sulfate scaling. Feed temperature has ranged from 24-30C and conductivity from 180-250 microsiemens-cm. The operations group at this plant decided to install one train of the new CPA5-LD on August 6, 2010 hoping to see a reduction in fouling and cleaning frequency and improved permeate quality. The 34-mil LD biostatic spacer would aid in the reduction of biological fouling, the 34-mil spacer would give reduced pressure drop and feed pressure and more effective cleanings, and the CPA5 membrane would result in better permeate quality. Table 3 shows that the membranes started up as projected.

Table 3: Startup data actual versus projected

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Projected</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed pressure</td>
<td>7.8 bar</td>
<td>7.85 bar</td>
</tr>
<tr>
<td>Pressure Drop (feed-to-conc)</td>
<td>1.3 bar</td>
<td>1.4 bar</td>
</tr>
<tr>
<td>Permeate TDS</td>
<td>1.1 mg/l</td>
<td>1.2 mg/l</td>
</tr>
</tbody>
</table>

As of January 5, 2011, the system has been operating well for 5-months with the CPA5-LD RO elements. There has been 3 scheduled cleanings in September, November and December and all have been effective in restoring the normalized data back near the baseline. The normalized permeate flow and normalized pressure drop are shown in Chart 5. The normalized permeate flow has held in a steady range of 105 to 120 m3/hr and all cleanings have resulted in normalize flow better than the 112 m3/hr baseline. The normalized pressure drop has seen increases up to 2.2 bar from a baseline of 1.6 bar, but the cleanings have effectively restored pressure drop back to baseline. The normalized % salt passage was initially 0.3% and after a month has stabilized at about 0.6%. The salt passage has been restored back to the 0.6% baseline after cleanings with excursions up to 1.2%. Reports from the field on January 21, 2011 indicated that they had observed the lowest conductivity to date from the train with CPA5-LD at 1.25 microsiemens-cm with other 1-2 year old trains running 2.4 to 5.4 microsiemens-cm.
Chart 5: Normalized Permeate Flow and Pressure Drop

Chart 6: Normalized % Salt Passage of the Permeate
CONCLUSION

This paper bears witness that there have been improvements in the ability to treat and purify difficult water sources to meet the needs of the Chilean copper mining industry. Advances in RO membrane technology have made the purification of water more reliable and cost effective by addressing the issues of fouling. The LD Technology has developed a RO feed spacer with biostatic properties to reduce the rate of biological fouling and the new geometry 34-mil spacer has addressed how to reduce the rate of colloidal fouling and make for more efficient and less frequent cleanings. The new CPA5-LD membrane has resulted in the best rejecting membrane of organic and inorganic components, particularly silica and nitrate. Operating costs will be realized by reducing energy costs, membrane replacement costs, better permeate quality, reduced chemical and labor costs resulting from fewer cleanings.

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