Extreme Recovery Membrane Process and Zero Liquid Discharge Low Temperature Crystallization for Treating Scaling Mine Waters

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Abstract

The paper describes a step change mine water treatment process that increases water recovery from 40-70% to over 95% without the use of chemical softening in a low cost membrane system. The cost of mine water treatment is decreased by eliminating chemicals and the hassles of chemical and sludge handling and reducing the highly expensive downstream evaporative brine management stage. The membrane process beneficially removes all contaminants of concern, unlike biological treatment where only specific ions are removed. Moreover, the membrane process can start instantaneously, is not temperature dependent, and can operate with fluctuating feed water chemistry. Full analytical results, performance and economics will be presented for an innovative Salt Splitter Reverse Osmosis process treatment of scaling mine waters. Results for a low temperature crystallizer and an advanced targeted removal process for nitrates are also presented.

Key words: Mine water, run-off, tailings, brackish, hardness, water treatment, electrodialysis, reverse osmosis, evaporator, crystallizer, calcium, sulfate, nitrates, selenium, cadmium, zinc

Introduction

The Salt Splitter Reverse Osmosis system offers mine operators an economical alternative to biological treatment systems. It provides reliable treatment of mine waters without intolerance of fluctuating temperature or feed chemistry of biological plants. It also beneficially removes all contaminants of concern rather than a select ion that is specific to that biological culture. As will be shown in this paper, the Salt Splitter Reverse Osmosis process demonstrated extreme high recovery of 96% operating on a highly calcium sulfate scaling mine runoff water. This reduces the brine discharge volumes by 90% compared to lime softening followed by reverse osmosis. It also eliminates large tanks, chemical material handling equipment, and sludge disposal associated with lime softening. The SS-RO reduces overall projects costs by reducing the cost of the more expensive brine management systems.

Mine operators seek economical, reliable treatment of tailings and run-off waters for contaminants of concern, such as selenium and other heavy metals, spanning the entire mine lifecycle. Biological treatment methods are appealing due to lack of brine discharge. However, recent results from full-scale treatment plants have shown inconsistent and unreliable performance, largely due to challenges in fluctuating feed water chemistry and low temperature.

Reverse osmosis (RO) is typically the lowest cost treatment method. However, due to the high scaling potential of many mining and hard brackish groundwater and industrial wastewaters, the performance and recovery of RO systems is often limited. Scale precipitates on the surface of the membrane, resulting in plugging of element feed passages and potential membrane damage. Frequent, costly, and time consuming cleanings are required to operate on these scaling waters.

The scaling potential of these waters is due to presence of sparingly soluble multivalent salts. Scaling occurs when a multivalent anion (SO_4^{2-} or CO_3^{2-}) pairs with a multivalent cation (Ca^{2+}, Mg^{2+}, Ba^{2+}, or Sr^{2+}) forming low solubility compounds such as $CaSO_4$, $CaCO_3$, and $BaSO_4$. The multivalent cations contribute to water hardness.

Conventional lime and ion exchange softening are often used for hardness removal. Lime softening has costs associated with chemical procurement, handling, and added safety risk as well as a sludge by-product. Ion exchange softening has high costs associated with regeneration due to chemicals and disposal of spent regeneration fluid.

Salt Splitter Reverse Osmosis (SS-RO) enables extreme recoveries on highly scaling waters, such as mine discharge and hard brackish water and wastewaters. An ion exchange membrane separation process produces two non-scaling streams from a single stream with high scaling potential. This separation process is followed by reverse osmosis. This lowers total project costs by eliminating chemical softening and reducing expensive downstream brine management requirements: smaller ponds, less deep wells, and lower capacity evaporative and crystallizer systems.

The Salt Splitter leverages electrodialysis, an industrial technology, for scale through addition of membrane packaged stacks (Figure 1). Electrodialysis operates by using a direct potential to flux dissolved salts through ion exchange membranes with water flowing parallel to the membranes. It operates at 100 kPa without pressure differences across the ion exchange membranes. This, along with water not being fluxed through the membranes, makes electrodialysis tolerant to inorganic scaling and organic fouling.

The main difference between electrodialysis and Salt Splitter is the SS uses specialized mono-selective ion exchange membranes for splitting the scaling salts and a proprietary process and control. These specialized ion exchange membranes have monovalent ion selectivity of up to 98% to facilitate the salt splitting process.

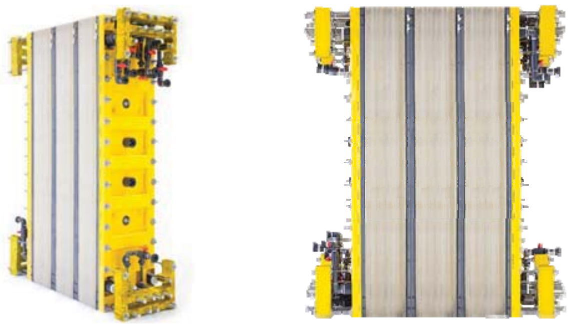

Figure 1: *Electrodialysis Membrane Packaged Stack*

The SS-RO eliminates the scaling potential of hard water. It works by separating multivalent cations from multivalent anions (Figure 2). Ions are transported from the process stream to form two separate highly concentrated brines. Partially electrochemical pre-treated water is fed to an RO unit, with the RO brine re-circulated to the Salt Splitter feed. A small portion of the RO brine is bled to prevent accumulation of organics.

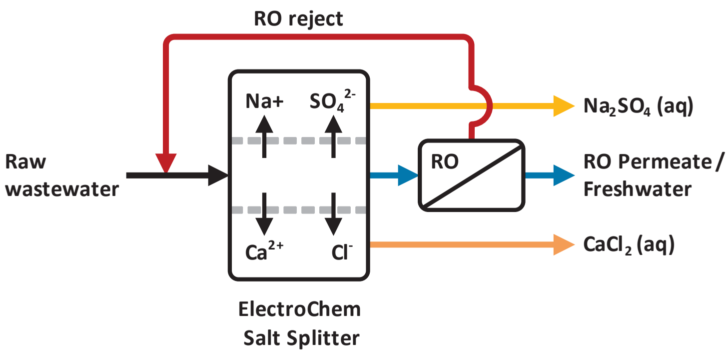

Figure 2: *Salt Splitter Reverse Osmosis Simplified Process Flow Diagram*

A feed water containing calcium sulfate and sodium chloride can be split into two non-scaling streams: one containing sodium sulfate (Na_2SO_4) and one containing calcium chloride ($CaCl_2$). Both of these streams have a solubility limit nearly 10 times that of calcium sulfate, 195,000 mg/L at 20°C compared to calcium sulfate at 2,550 mg/L at 20°C (Figure 3). This represents a potential brine concentration that is 75 times higher and results in a system that can recover over 96% of the feed water without scaling.

The SS-RO process softens water which allows reverse osmosis to operate at much higher reliability. The RO is fed with Salt Splitter product that has most of the scaling salts removed. The RO further desalinates the product water and produces a high quality RO permeate. The RO brine is sent back to the Salt Splitter for further concentration. Two highly concentrated low volume brines, with the scaling ions largely separated, are produced by the electrochemical Salt Splitter unit.

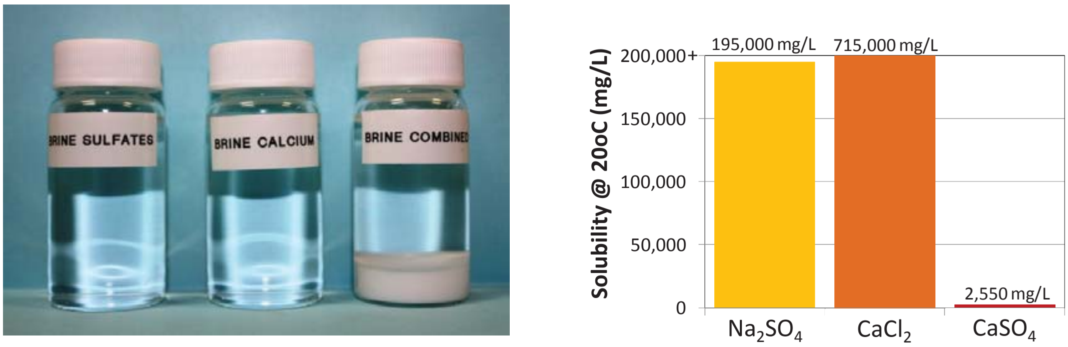

Figure 3: *Solubility Limits of $CaCl_2$ and Na_2SO_4 Solutions*

SS-RO brine can be treated with a low temperature crystallizer for true zero liquid discharge (ZLD). True ZLD is defined as producing only freshwater and solids from the process water. ZLD is practiced when projects have no access to ponds or deep wells and trucking great distances for disposal is too expensive.

The low temperature crystallizer uses a four effect humidification-dehumidification (HDH) cycle to concentrate wastewater or brine to greater than 30% solids by mass and produce freshwater (Figure 4). It is designed to operate on scaling and challenging fluids. Moderate grade heat (i.e. 90°C) generated from waste heat or natural gas, is used to evaporate and condense the wastewater in successive "effects". Latent heat of condensation is recycled as it is downgraded four times. This produces distilled water and requires only one quarter the heat required by conventional, open to atmosphere evaporators. It produces a highly concentrated brine or solids for true zero liquid discharge.

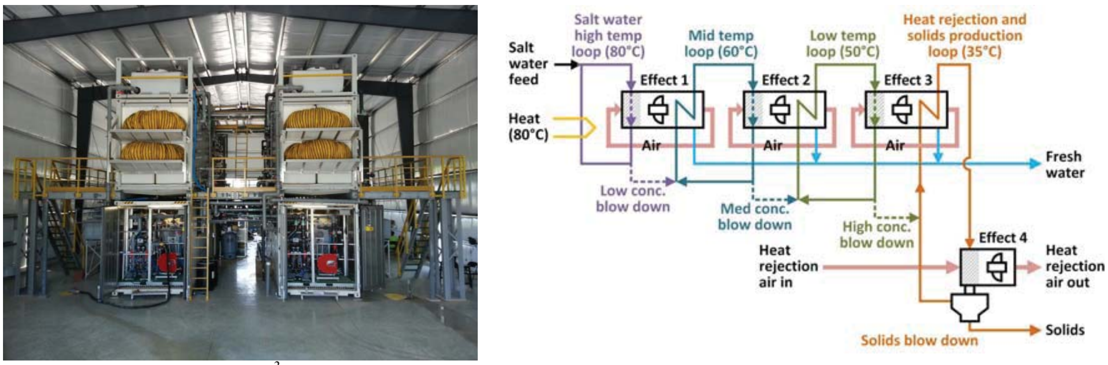

Figure 4: *100 m^3/day Low Temperature Crystallizer (left) and Simplified PFD (right)*

Project Overview

A small Salt Splitter Reverse Osmosis pilot project (~80 L/day) was completed for a Canadian miner. Runoff from the mine required treatment for contaminants of concern, such as sulfate, selenium, and other heavy metals. The runoff was predominantly gypsum salts near saturation. Calcium and sulfate comprised 71% of the runoff's's total dissolved solids (Table 1). The mine runoff contained relatively few monovalent ions. The Salt Splitter process requires sufficient monovalent ions to split scaling $CaSO_4$ into non-scaling $CaCl_2$ and Na_2SO_4. Sodium chloride was used to supply the required monovalent ions to complete the salt splitting process. Sodium chloride represents approximately 10% of the total cost of treatment.

Table 1: *Mine Run Off Water Chemistry*

Parameter (mg/L)	RAW Mine Runoff Water
pH	7.60
Total Dissolved Solids	4048
Total Hardness (as CaCO3)	3082
Alkalinity (as CaCO3)	593
Calcium	507
Chloride	23.2
Magnesium	442
Sodium	18.5
Sulfate	2369

The miner previously pilot tested conventional membrane based systems to treat the runoff. This included the following:

- Lime Softening followed by RO achieving 65% recovery. This process required the use and handling of chemicals and management of sludge waste.
- Electrodialysis Reversal softening followed by RO (EDR-RO Hybrid) achieving 80% recovery. This process did not require chemical addition or produce sludge. EDR is not a pressurized filtration process. Thus water is not being fluxed through the membrane, and it is more tolerant of inorganic scaling and organic fouling than reverse osmosis. However, the recovery of the EDR-RO hybrid plant is still limited by the concentration of $CaSO_4$ in the brine stream. Even using antiscalants and advanced EDR cleaning systems, the brine concentration is limited to four times the solubility limit of $CaSO_4$.

Previous piloting results showed that the maximum recovery for the EDR-RO hybrid process for this application is 80%. A 20,000 m^3/day plant would produce 4,000 m^3/day of brine to be managed. Managing this volume of brine increases the overall project costs. Therefore, a low cost process to reduce brine discharge volumes would significantly reduce total project costs.

Project Objectives

The objective of the pilot project was to demonstrate that the SS-RO process can reduce brine volume and operate reliably on a high scaling mine water. Specific objectives were as follows:

- Determine the size of the full sized plant by determining the brine concentration limits
- Produce high quality RO permeate that meets regulatory discharge requirements.
- Demonstrate pilot plant reliability by operating continuously.

Pilot Plant Description

The SS-RO project was completed on Saltworks' small pilot plant. Capacity ranges based on stack size and test water availability. This projects capacity was set to produce roughly 80 L/day. The plant is an integrated Salt Splitter Reverse Osmosis system with full automation and data acquisition (Figure 5).

The plant has internet login capabilities for remote monitoring and operation of the system. The runoff was pretreated with 50 µm and automatically acidifed to remove particles and reduce carbonate scaling risk.

Figure 5: *Salt Splitter Stack (left), Salt Splitter Reverse Osmosis Hybrid Pilot (middle and right)*

Project Results

The SS-RO pilot achieved 96% recovery, met regulatory discharge requirements, and operated continuously for more than 1,500 hours (60 days). The SS-RO treated 5,300 L of water producing 5,100 L of permeate. Approximately 100 L of Na_2SO_4 brine, and 100 L of $CaCl_2$ brine, both with TDS > 120,000 mg/L, were produced.

Extreme Recovery

Brine concentrations of greater than 120,000 mg/L TDS were produced from mine runoff water near calcium sulfate saturation. The two brine streams steadily increased in concentration and then plateaued at a conductivity limit of ~130 mS/cm (Figure 6).

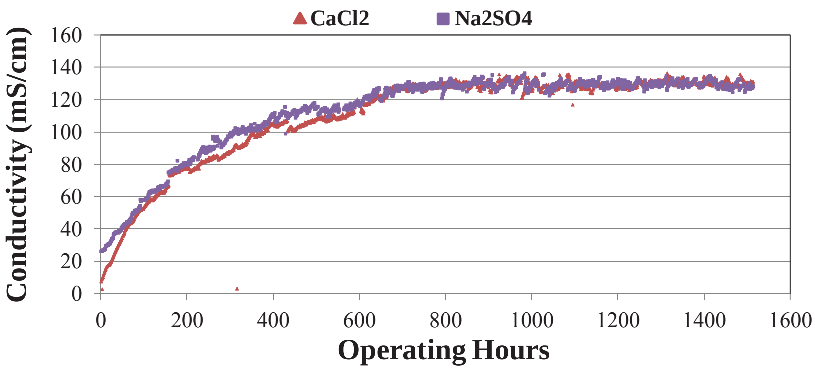

Figure 6: *Achieving High $CaCl_2$ and Na_2SO_4 Brine Concentrations*

Samples of the two brines at steady state were collected and submitted to an independent laboratory for analysis. The laboratory results for the two streams are summarized in Table 2. Results show the following:

- The TDS of both brines are >120,000 mg/L.
- The Salt Splitter successfully separated the $CaSO_4$ solution into two non-scaling brines
  - The $CaCl_2$ brine has sulfate concentrations <300 mg/L
  - The Na_2SO_4 brine has hardness <200 mg/L as $CaCO_3$
- The pH of both brines were <5, due to acid dosing to mitigate carbonate scaling risk. Minimal NaOH or lime would be required to neutralize the pH of these brines.

Table 2: *Salt Splitter Brine Chemistry for $CaCl_2$ and Na_2SO_4*

Parameter (mg/L)	RAW Mine Runoff Water	Salt Splitter $CaCl_2$ Brine	Salt Splitter Na_2SO_4 Brine
pH	7.60	3.88	4.89
Total Dissolved Solids	4048	125000	157000
Total Hardness (as CaCO3)	3082	65700	176
Alkalinity (as CaCO3)	593	<1	1
Calcium	507	10200	39
Chloride	23.2	67400	37600
Magnesium	442	9770	19
Sodium	18.5	13800	59200
Sulfate	2369	297	64100

Meeting Discharge Limits

The RO produced 5,100L of permeate from 5,300L of mine runoff water. A sample of the RO permeate was submitted to an independent laboratory for analysis. The results are summarized in Figure 7 and are compared to regulatory discharge limits. Key results are as follows:

- High quality RO permeate was produced with a TDS of 18 mg/L
- All regulated parameters met discharge requirements

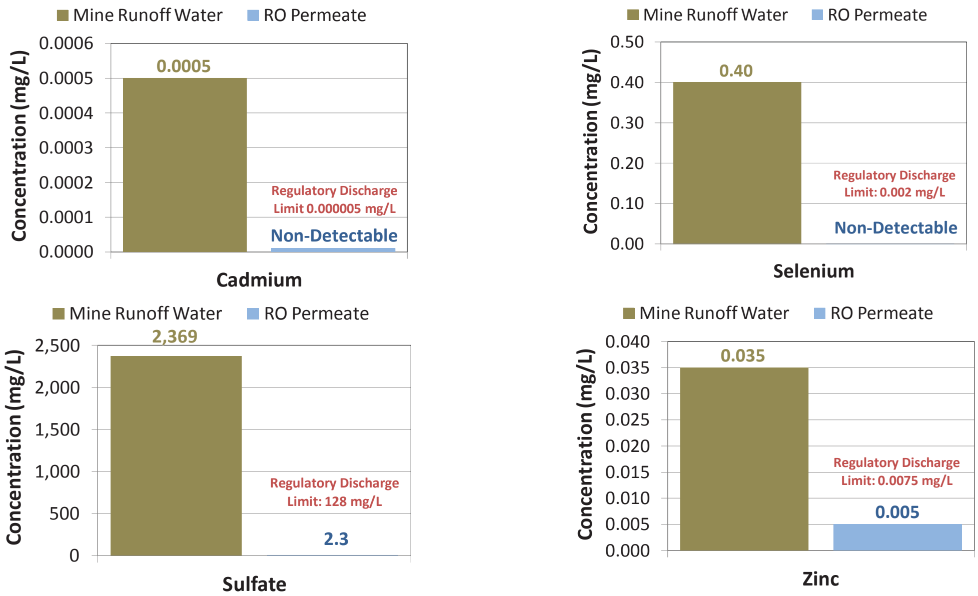

Figure 7: *RO Permeate Water Chemistry Compared to Regulatory Discharge Limits*

Reliable Operation

The SS-RO pilot went through a series of trials to find brine concentration limits and refine process controls specific to this mine water. In the final test run, the plant was operated continuously for over 1,500 hrs (60 days) and continues to operate at the time of writing.

Low Temperature Crystallizer

The high solubility, low volume SS-RO brines were to be treated with a low temperature crystallizer for additional freshwater and solids production. However, since the SS-RO operated at 96% recovery, there was not enough brine produced to pilot the crystallizer at the time of writing. Table 3 and Figure

8 show typical freshwater data and ZLD solids pictures for the low temperature crystallizer from projects completed on shale gas produced water, landfill leachate, and oil sands produced water evaporator blowdown.

Table 3: *Exemplary SaltMaker Feed Water and Freshwater Quality*

	Oil Sands Evaporator Blowdown		Shale Gas Produced Water		Landfill Leachate	
Parameter (mg/L)	Raw	Freshwater	Raw	Freshwater	Raw	Freshwater
Total Dissolved Solids	66,300 to 147,000	103	54,600 to 230,000	95	12,000 to 90,500	135
Total Hardness (as CaCO3)	229 to 725	<2	725 to 41,200	5	500 to 14,000	5

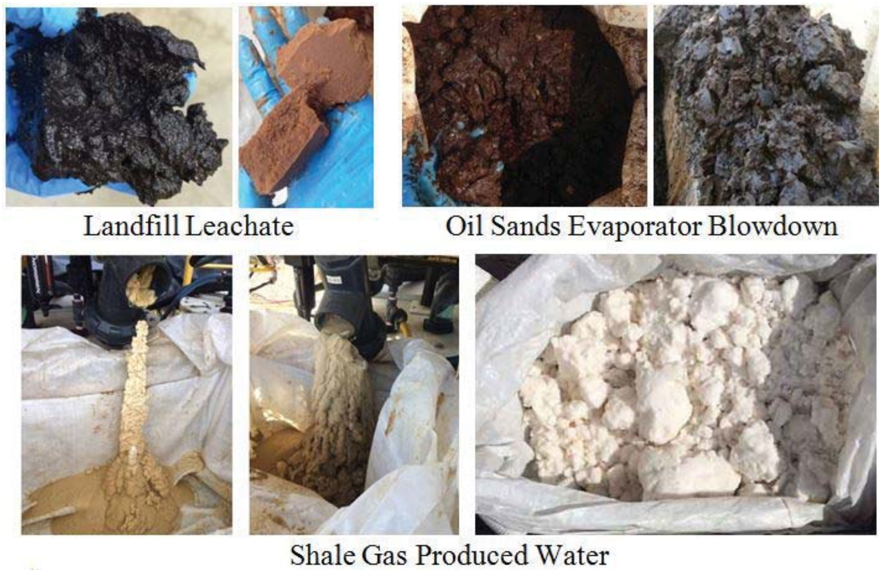

Figure 8: *Low Temperature Crystallizer True ZLD Solids*

Nitrate Removal

The project also demonstrated selective nitrate removal with 97% recovery. The miner operates a biological system to remove selenium from their run off. Nitrate concentration spikes in the feed water reduce treatment efficiency. Nitrates, due to explosives residuals, in the mine runoff were treated by adapting the advanced electrodialysis system for selective nitrate removal (EDR-N). The EDR-N system uses the same equipment with a different configuration of membranes. The test results show that it reduces nitrate concentrations from 131 mg/L as N down to 5.3 mg/L as N (Table 4). 97% recovery was achieved by concentrating the nitrate in the brine to over 4800 mg/L as N. EDR-N selectively removes nitrates (96% removal) with ion specific ion exchange membranes (Figure 9).

Parameter (mg/L)	**Raw Mine Runoff Water**	**EDR-N Product Water**	**EDR-N Brine**
pH	7.60	8.22	7.70
Total Dissolved Solids	4048	2780	47800
Hardness (as CaCO3)	3082	1860	32100
Calcium	507	300	5980
Magnesium	442	270	4160
Nitrate (as N)	131	5.29	4830
Sulfate	2370	2350	3570

Table 4: *EDR-N Water Chemstry Demonstrating Selective Nitrate Removal*

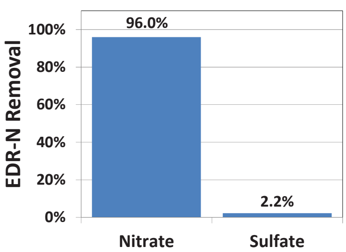

Figure 9: *EDR-N Selective Nitrate Removal*

The brine from the EDR-N system can also be treated by a low temperature crystallizer for true ZLD. The brine is a predominantly nitrate/calcium/magnesium solution. Results show that the brine can be solidified and encapsulated to pass the necessary leaching tests to meet non-hazardous landfill acceptance criteria for final disposal.

Economics

The total cost of ownership for the SS-RO-Low Temperature Crystallizer treatment process is estimated at \$3 USD/m^3 plant inlet, assuming efficient construction, 8% interest rate, and 10 year project life. Lifecycle costs are based on the small pilot test results and for a full-scale plant capacity of 20,000 m^3/day. The lifecycle costs are summarized in Table 5.

Table 5: *Economics for a 20,000 m^3/day Salt Splitter Reverse Osmosis Crystallizer Plant*

SS-RO	Capex (includes site construction)	\$0.99/m^3 plant inlet
	Opex (labor, maintenance, and consumables)	\$0.41/m^3 plant inlet
	Opex (NaCl)	\$0.20/m^3 plant inlet
	Opex (Energy)	\$0.26/m^3 plant inlet
Low Temperature Crystallizer	Capex	\$0.80/m^3 plant inlet
	Opex (Non-Energy)	\$0.14/m^3 plant inlet
	Opex (Energy)	\$0.17/m^3 plant inlet
Total Cost of Ownership (SS-RO-Low Temperature Crystallizer)		**\$2.97/m^3 plant inlet**

Conclusions

The Salt Splitter Reverse Osmosis system offers mine operators an economical alternative to biological treatment systems. It provides reliable treatment of mine waters without intolerance of fluctuating temperature or feed chemistry of biological plants. The Salt Splitter Reverse Osmosis process demonstrated extreme high recovery of 96% operating on a highly scaling mine runoff water. This reduces the brine discharge volumes by 90% compared to lime softening followed by reverse osmosis. It also eliminates large tanks, chemical material handling equipment, and sludge disposal associated with lime softening. High quality RO permeate was produced that met regulatory discharge limits. The SS-RO reduces overall projects costs by reducing the cost of the more expensive brine management systems. The non-scaling brines can be treated by a low temperature crystallizer for true zero liquid discharge and a complete cradle to grave solution. Total cost of ownership for a Salt Splitter Reverse Osmosis and Low Temperature Crystallizer treatment process is USD \$3/m^3 plant inlet.

The advanced electrodialysis system can also be adapted to remove nitrate spikes from the feed of existing biological systems. EDR-N selectively removes nitrates from 130 mg/L as N to 5 mg/L as N to improve existing biological plants' performance and reliability. High recovery of 97% reduces brine volume and minimizes the costs of a downstream low temperature crystallizer for true ZLD.