A Cradle to Grave Treatment Solution for Mine Waters

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Abstract

The global mining industry is seeking economical tailings treatment options. The paper introduces two step change technologies for cradle-to-grave mine waters treatment and zero liquid discharge (ZLD). ZLD is defined as only two plant outputs: (1) treated water meeting specification; (2) all contaminants reduced to a solid for final disposal. The innovative technologies that will be presented are a salt splitting electrodialysis – reverse osmosis hybrid and a non-metallic, low temperature (<90°C) crystallizer. The presented treatment solutions are applicable to treating any mine waters, such as tailings, runoff, and acid mine drainage. It provides an end-to-end treatment process with recovery of freshwater and final landfill disposal of the residuals.

Keywords: water treatment, tailings, runoff, acid rock drainage, acid mine drainage, ARD, AMD, softening, reverse osmosis, RO, zero liquid discharge, ZLD, electrodialysis, ion exchange, evaporator, crystallizer, desalination.

Introduction

An innovative mine water treatment system is presented that achieves extreme recoveries and a 45% total cost of ownership savings over conventional lime - soda ash - reverse osmosis (RO) – evaporator - crystallizer systems. The system is based around reverse osmosis (RO) hybridized with electrodialysis. The novel process and modified electrodialysis system changes water chemistry from highly scaling to non-scaling by use of selective ion exchange membranes. The water chemistry is changed from, for example, scaling calcium sulfate into non-scaling calcium chloride and sodium sulfate. This eliminates the need for expensive soda ash softening and associated hassles of sludge management. The ion exchange membrane system also concentrates the RO brine to extreme levels previously only attainable by thermally driven processes (≈200,000 mg/L TDS). The result is both lower operating costs and reducing the brine volume by two thirds using a membrane system. Importantly, this results in smaller capacity downstream evaporators lowering project costs. A case study and economic analysis are presented whereby savings of up to 45% in total cost of ownership are achieved. These savings result from a 25% reduction in capital and 37% reduction in operating costs relative to above referenced conventional treatment train.

Scaling Management

Mine waters vary widely but most contain the following types of scalants:

- Low solubility metals, such as iron, nickel, cobalt, and aluminum, can create scaling compounds but can be readily precipitated by raising pH via caustic or lime addition;
- Low solubility anions, such as fluoride, phosphate, and sulfate, can combine with calcium to create scale and are not readily removed to reliable levels through precipitation, thus requiring further management;
- Divalent cations responsible for high hardness, primarily calcium and magnesium, as well as barium and strontium. Elevating pH will precipitate magnesium but has little effect on calcium, barium or strontium unless carbonate is present.

Conventional Treatment Process

Although mine water chemistry varies between sites, there are common treatment systems that are employed (Table 1).

Table 1 Mine water Conventional Treatment Processes

Process	Description
Lime (calcium hydroxide) softening	Removes magnesium hardness and heavy metals. Some calcium is removed but only calcium that is "associated" with carbonate.
Soda ash (sodium carbonate) softening	Removes calcium hardness. The cost of soda ash can account for over 20% of the treatment total cost of ownership (capital plus operating cost).
Ion exchange	Employs resins to adsorb calcium, reducing calcium levels to less than 50 mg/L. However, the resins must be regenerated with acid, resulting in high operating costs and acidic chemical waste that requires disposal.
Reverse Osmosis (RO)	The most dominant and widely practiced desalination technology for removal of total dissolved solids (TDS). RO is low cost but requires notable chemical pre-treatment for reliable operation on mine waters. When operated on scaling ion chemistry, RO is susceptible to fouling and does not concentrate well past 60,000 mg/L. This results in low recoveries and high brine volumes (or very frequent chemical cleans). Any RO unit can be hybridized with the innovative treatment system presented in this article.
Thermal brine management (evaporator, crystallizer, SaltMaker)	Evaporators concentrate the final brine waste and crystallizers produce solids. These systems are required for brine management and ZLD – and are the most expensive process equipment in the treatment train in terms of both capital and energy cost. The required capacity and energy used by these systems can be reduced if the recovery of upstream membrane system is increased. Membrane systems are often 5-10 times lower cost per unit volume processed and therefore it makes sense to maximize their recovery.

Salt Splitter-RO: High Recovery Mine Water Treatment System

A mine water treatment solution was developed by Saltworks Technologies that builds on the past work of Toshikatsu Hamano (1993) and Thomas Davis (2008). Hamano's original concept in 1993 was a desalination process comprising of two electrodialysis stages that permanently changed low-solubility calcium sulfate into highly soluble calcium chloride and sodium sulfate. Solubility of these ion pairs is shown in Figure 1 (low solubility means greater scaling risk). Davis worked on a similar process in 2008 when he developed an electrodialysis metathesis (EDM) process for feed waters comprised solely of calcium sulfate.

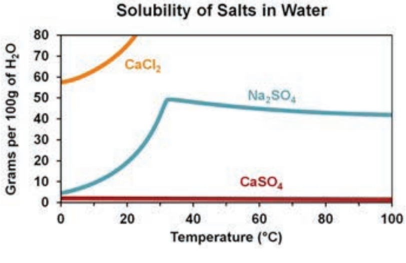

Figure 1 Solubility of $CaSO_4$, Na_2SO_4, and $CaCl_2$

Saltworks' Salt Splitting system expands on this work with several proprietary innovations – monovalent selective ion exchange membranes process, and controls – that enable an industrially applicable treatment plant. The technology is built around hybridizing two common desalination technologies: electrodialysis (ED) and reverse osmosis (RO). The advanced salt splitting electrodialysis unit acts as a turbocharger for the RO. It removes scaling limits by permanently changing water chemistry: divalent scaling low solubility ion pairs such as calcium sulfate are "split" into non-scaling high solubility ion pairs such as sodium sulfate and calcium chloride. The RO unit operates on an electrochemically softened feed, at a greater reliability level and lower pressure than conventionally possible. The combined ED-RO hybrid produces two highly soluble output brines with a combined average brine concentration of ≈210,000 mg/L TDS. These can be sent to separate downstream processing stages for volume reduction or solidification. A simplified electrodialysis stack arrangement diagram, showing how the ions are selectively transferred into separate brine compartments to produce non-scaling Na_2SO_4 and $CaCl_2$ (Figure 2).

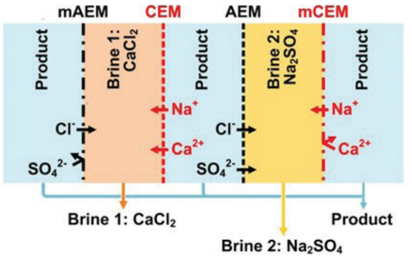

***Figure 2** Salt Splitting Electrodialysis*

The salt splitting ED-RO hybrid provides the following benefits:

- Recovery of the membrane system is three times that of chemically softened RO, while eliminating the need for expensive soda ash softening;
- Improved RO reliability and reduced operating costs from lower pressure requirements;
- The non-scaling, lower volume brines reduce the need for chemical softening of the evaporator inlet and allow downsizing of brine management assets;
- Less residual waste mass is produced since soda ash addition is eliminated and because useful by-products, such as sodium sulfate, can be recovered from the waste.

Shown below are modular salt splitting electrodialysis stack (Figure 3), containerized pilot (Figure 4), RO (Figure 5), and Saltworks' proprietary highly selective membranes (Figure 6).

SaltMaker for Zero Liquid Discharge: Low Temperature Evaporator Crystallizer

The SaltMaker is a non-metallic, low temperature (<90 °C) crystallizer that achieves zero liquid discharge (ZLD) (Figure 4). It is a one-step treatment plant (no chemical softening) for a complete cradle-to-grave mine water treatment solution. The crystallizer enables ZLD through:

1. Multiple effect evaporation with low grade heat recycle reducing energy consumption. The SaltMaker can use a variety of thermal sources: steam, low grade waste heat, and gas or liquid fuel fired low pressure water heaters. It operates at atmospheric pressure and temperatures less than 90°C, employing humidification dehumidification air cycles that do not require a vacuum, pressure, or boiling water on any heat transfer surfaces.
2. Modular design based on engineered plastics and built-in redundancy. The SaltMaker is predominantly built from gel-coated, fibre-reinforced plastics – with low surface energy that provides resistance to corrosion and scale. The plant has redundant process sets for no single point of failure.
3. Advanced automation and self-cleaning. The plant's self-cleaning modes prevent irreversible scaling or fouling by regularly

***Figure 3** (left to right) Salt Splitting Stack, ED-RO pilot, RO elements, and salt splitting ion exchange membrane*

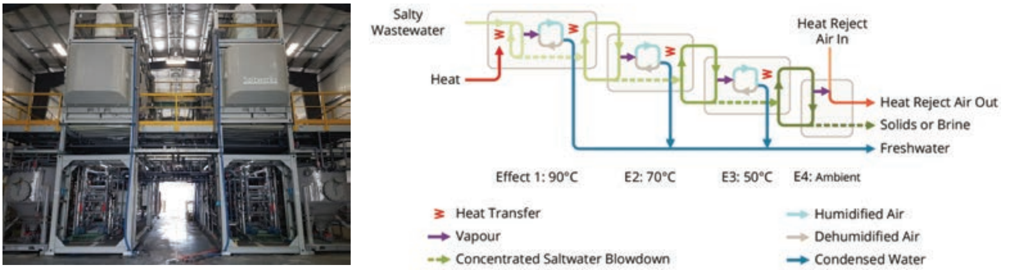

Figure 4 *SaltMaker Crystallizer (left) and simplified process flow diagram (right)*

monitoring key performance metrics. It will then automatically trigger the appropriate level of cleaning, from 'light rinse' to 'heavy scrub'. The SaltMaker uses distilled water as the cleaning fluid, which can be chemically augmented based on the type of scaling compounds and foulants in the brine. The wash solution is reused multiple times before being fed back to the SaltMaker for treatment once it has been spent.; and

4. A simplified solids extraction and bagging process. A circulating slurry continuously forms and grows crystals in the SaltMaker. Solid salt is discharged to an automated bagging system which dewaters the solids to pass paint filter tests for landfill disposal.

Case Study

A fully automated salt splitting ED-RO pilot plant was operated on a coal plant wastewater, with the following objectives:

1. Confirm treated discharge water quality;
2. Confirm membrane system recovery, reliability, chemical and energy consumption; and
3. Develop economics for a full-scale system, including a downstream evaporator-crystallizer.

The treatment process is shown schematically in Figure 5 below. Pre-treatment for the reverse osmosis unit is required, such as multimedia filtration or ultrafiltration.

Detailed analytics for all streams are shown in Table 2 and compared to the discharge regulations.

The salt splitting ED-RO hybrid successfully treated the coal plant wastewater to meet the discharge regulations. The pilot plant operated continuously for 90 days. Freshwater recovery of 90% was achieved from the membrane system, with no soda ash softening. In comparison, chemically softened RO system projections showed a recovery of approximately 70%. Put another way, the ED-RO system produced one third the brine reject volume or 67% less brine, requiring a 67% smaller evaporator system. The ED-RO hybrid generated non-scaling, high concentration, low volume brines. Most importantly, two non-scaling brines were produced in excess of 200,000 mg/L, which is brine con-

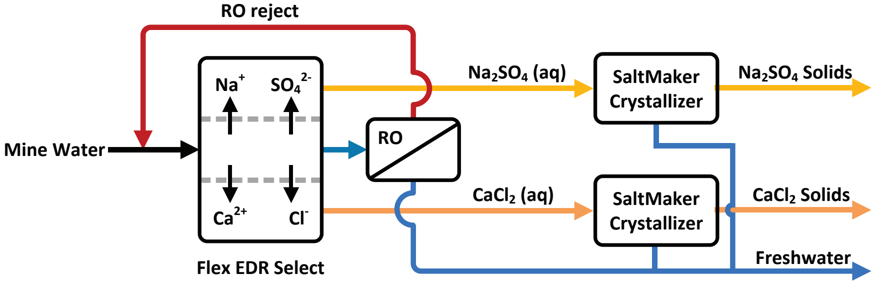

Figure 5 *Salt splitting ED-RO-SaltMaker process*

***Table 2** Salt splitting ED-RO treatment of FGD wastewater: water chemistry results*

Parameter (mg/L)	Coal Plant Wastewater	$CaCl_2$ Brine	Na_2SO_4 Brine	RO Permeate	Discharge Regulations
pH	*7.02*	6.98	6.70	*6.52*	6 - 9
TDS	19300	220700	209700	120	N/A
Aluminum	*0.04*	0.01	<0.01	*<0.0001*	0.05
Arsenic	**0.45**	3.06	0.85	*<0.0001*	0.005
Cadmium	**0.11**	0.02	<0.01	*0.00010*	0.000005
Calcium	3290	73230	768	6.0	N/A
Chloride	**11050**	140300	93100	*23.2*	150
Cobalt	*0.00162*	0.0187	0.0011	*<0.00005*	0.004
Fluoride	**9.0**	7.8	0.34	*<0.05*	0.4
Iron	*0.11*	0.02	<0.01	*<0.01*	0.35
Lead	*<0.0002*	<0.0002	<0.0002	*<0.0002*	0.003
Magnesium	1850	1580	17.4	2.20	N/A
Mercury	**0.10**	0.02	0.0002	*<0.00001*	0.00001
Selenium	**0.28**	0.10	4.90	*<0.0005*	0.002
Sodium	663	2400	77400	9.3	N/A
Sulfate	**1945**	352	36620	*3.1*	128
Zinc	**1.52**	0.26	<0.01	*<0.0001*	0.0075

ITALIC indicates meets Discharge Regulations. **BOLD** indicates does not meet Discharge Regulations.

***Figure 6** (left to right) automater bagging system, bag removed by forklift, and bag of solids*

centration territory normally reserved for evaporators.

The high solubility, low volume salt splitting ED-RO brines can be treated with a low temperature crystallizer for additional freshwater and solids production. Figure 6 shows solids produced (10% moisture content that passes paint filter tests) by SaltMaker crystallizer for true ZLD.

Economics

The salt splitting ED-RO SaltMaker has an overall 45% total cost of ownership savings over a conventional chemical softening RO-evaporator-crystallizer treatment train for a 1090 m^3/day plant. This is due to savings of 25% in capital cost on the process equipment and savings of 37% by eliminating soda ash softening. An economic analysis is summarized in Table 3 based on the water chemistry shown in Table 2. It assumes that ZLD is required. Capital costs were based on US market prices for chemical softeners, industrial reverse osmosis, and evaporator-crystallizers. Only process equipment costs were accounted for in both options. Building and installation costs were not accounted for and assumed to be the same for both options. Capital costs were amortized over 10 years at an 8% discount rate. Plant availability was assumed to be 95%. Power costs were assumed to be USD$0.065/kWh and thermal energy costs at USD$3/MMBTU.

Table 3 *Economic Analysis Summary*

Performance Summary	Conventional: Soda-RO-Evap-Crys	Advanced: SS-RO-SaltMaker
Plant Inlet Capacity (m3/day)	1,090	1,090
Plant Inlet Capacity (tonnes/day)	1,123	1,123
Plant Inlet Total Dissolved Solids (TDS)	19,062	19,062
Membrane System Recovery	70%	90%
Size of Evaporation System (tonnes/day inlet)*	337	125
Size of Evaporation System (m3/day inlet)	327	104
Mass of Solids Produced (tonnes/day)	25	21
Performance Summary	**Conventional: Soda-RO-Evap-Crys**	**Advanced: SS-RO-SaltMaker**
Capital Costs		
Pre-Treatment & Membrane System	$ 2,788,634	$ 4,113,636
Evaporation-Crystallization System	$ 6,200,000	$ 2,650,000
Installation (assumed equal for both)	Not included	Not included
Sub-Total Capital Cost	**$ 8,988,634**	**$ 6,763,636**
Capital Cost ($/m3)	$ 3.68	$ 2.67
Energy Consumption Analysis		
Power: Pre-Treat & Membrane System (kW_e)	178	429
Power: Thermal System(kW_e)	501	60.4
Power: Total	679	490
Thermal Power as Low Pressure Steam (MW_t)	0.3	0.8
Thermal Power as Low Pressure Steam (tonnes/day)**	11.7	27.0
Operating Costs		
Labor (assumed equal for both)	Not included	Not included
Soda Ash ($/yr)	$ 1,125,857	$ -
Soda Ash ($/m3 inlet)	$ 2.98	$ -
Sodium Chloride ($/yr)	$ -	$ 14,740
Sodium Chloride ($/m3 inlet)	$ -	$ 0.04
Chemicals: Other ($/yr)	$ 41,799	$ 275,192
Chemicals: Other ($/m3)	$ 0.11	$ 0.73
Energy: Electrical ($/yr)	$ 386,013	$ 318,152
Energy: Electrical ($/m3 inlet)	$ 1.02	$ 0.84
Energy: Thermal ($/yr)	$ 110,753	$ 76,737
Energy: Thermal ($/m3 inlet)	$ 0.29	$ 0.20
Sub-Total Operating Cost ($/yr)	**$ 1,664,422**	**$ 670,082**
Sub-Total Operating Cost ($/m3)	$ 4.40	$ 1.77
Total Cost (Less Install & Labor) ($/m3)	**$ 8.09**	**$ 4.44**
Savings		
CapEx Savings From Increased Membrane System Recovery (%)		25%
OpEx Savings From Eliminating Soda Ash (%)		37%
Total Cost of Ownership Savings (%)		**45%**

**Density of the brine adjusted inlet volume. Salt Splitter ED-RO brines have high density with specific gravity of ~1.2*

*** Advanced option assumes a multiple effect thermally driven crystalizer driven with 95 deg C heat (SaltMaker)*

Conclusion

Changing regulations are driving both innovation and the uptake of mine water treatment solutions. Treatment approaches vary widely depending on the mine site and its particular water chemistry, flow rate, and discharge regulations. However, to optimize treatment economics, there are steps a mine or water treatment plant designer can take that are consistent across all facilities:

- Eliminate soda ash softening; and
- Increase membrane system recovery to reduce size of thermal evaporation technologies.

The case study and economic comparison presented demonstrate the salt splitting ED-RO hybrid's ability to achieve these objectives.

References

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