Novel salt extractor system for salt removal from mine water and calcium sulfate removal on the International Space Station

Benjamin Sparrow, Malcolm Man, and Joshua Zoshi

Saltworks Technologies Inc., 2105 Commissioner St., Vancouver, BC, Canada, info@saltworkstech.com

Abstract

A novel salt extractor technology is presented. It was developed to remove salts and produce freshwater from large volumes of low salinity water commonly encountered in mining. The salt extractor is a hybrid of electrochemical separation and humidification-dehumidification (HDH) zero liquid discharge technology. It removes salts from the water balance. A similar front-end electrochemical system was procured by NASA for testing and possible future application on the International Space Station to increase water recovery in conjunction with their onboard crystallizer.

The presented work first reviews the dominant inland desalination method: reverse osmosis (RO) followed by concentrator-crystallizers. The salt extractor process is described, compared, and contrasted. Conclusions show the proposed system may provide a lower cost alternative to a combined RO and crystallizer system. Recommended next steps for development and piloting are discussed.

Background

Water is widely used in mining. Regulations are tightening and the cost of water management is increasing. Desalination technology is being adopted to desalt brackish mine water, remediate tailings, and treat acid rock run-off. These saltwater sources represent large volumes of water with very low salt levels, commonly less than 1% salt by mass (<10,000 ppm). The low salt content makes the water unfit for re-use or discharge. If the salt was removed it would offer two benefits: (1) ability to "close the loop" and re-use the water resulting in reduced wastewater volumes and tailing impoundment requirements; and (2) reduced freshwater withdrawal requirements; both of which would ease permitting risk.

Miners are starting to adopt reverse osmosis (RO) for brackish mine dewatering and chemical precipitation for acid rock drainage. Chemical precipitation, such as lime softening, entails large volumes of chemical procurement, handling, and sludge disposal which add safety liabilities and costs. Reverse osmosis (RO) is a dominant low cost and reliable seawater desalination technology and is increasingly practiced in mine dewatering if the water is low in organic content and has pH within range (often pH 2-10).

Reverse osmosis (RO) fluxes water through a semi-permeable membrane, as depicted in Figure 1, resulting in brine with 4% to 8% salt mass concentration. For most inland brackish water scenarios, 75% RO recovery is achievable. This means that the brine volume equates to 25% of the inlet volume. Higher concentration, lower volume brines are generally preferred as this reduces the capacity of the more expensive downstream brine management option.

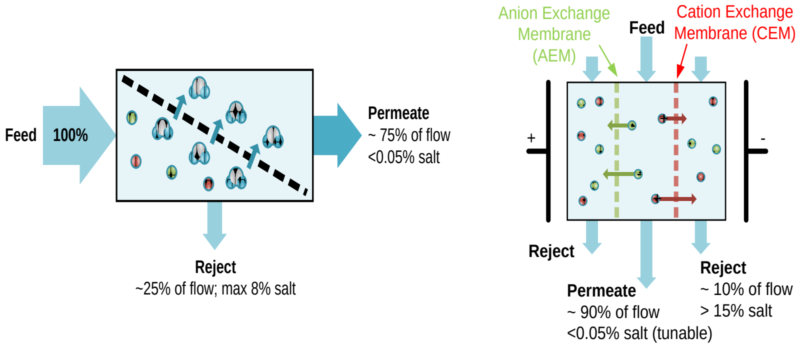
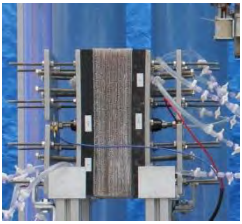


Figure 1 *Reverse Osmosis and Electrodialysis Comparison*

Electrodialysis is compared with RO in Figure 1. Rather than fluxing a mass of water through a semi permeable membrane, electrodialysis fluxes a lower mass of salt (often 1% by mass relative to water) through an ion exchange membrane. A direct current potential is applied via electrodes, forcing positive ions such as sodium and calcium through cation exchange membranes in one direction and negative ions such as chloride and sulfates through anion exchange membranes in the opposite direction. The membranes can be de-scaled by reversing polarity of the electrodes, through a technique known as electrodialysis reversal (EDR). EDR periodically drives salts in an opposite direction through the membrane, simultaneously de-scaling and maintaining product water production.

An electrodialysis apparatus may take the form of a “stack” of alternating membranes and gasket separators. Figure 2 shows several such apparatus, including a smaller test-scale “toaster” sized stack alongside a larger “refrigerator” sized modular stack. The smaller stack can process up to 200 L/day and is of the type being tested by NASA. The larger stack modules can process up to 50,000 L/day each, depending on salinities, and are designed such that two rows of multiple modules will fit inside a single intermodal shipping container for high capacity modular dispatch. Both can be configured to use the High Concentration Electrodialysis reversal (HC-EDR) process disclosed below.



Test scale HC-EDR stack

HC-EDR test jig

Large stack modules

Stack assembly & frames

***Figure 2** Sample Electrodialysis Stack*

Salt Extractor Process Introduction

The "Salt Extractor" is a new process involving a hybrid electrochemical and solids salt production plant and intended for low cost treatment of large volumes of water. A simplified schematic is shown in Figure 3.

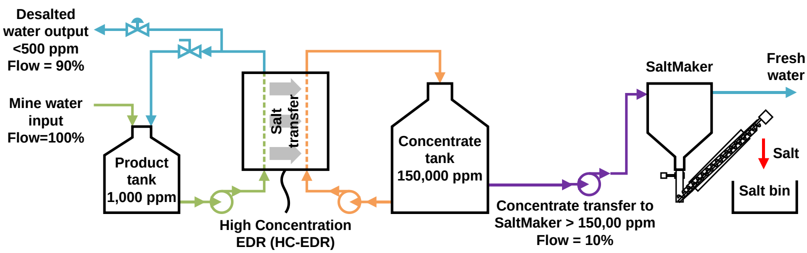


***Figure 3** Hybrid High Concentration Electrodialysis reversal (HC-EDR) with HDH SaltMaker plant*

A High Concentration Electrodialysis reversal (HC-EDR) device transports salt to a concentrated brine at 15% salt mass (15,000 ppm). This brine is more than twice the highest concentration achievable by RO and as a result half the volume. The 15% brine is then treated in a heat pump driven HDH system to concentrate it first to saturation and then solids whilst producing additional freshwater.

Mine Water Representative Data

Canada's oil sands in Northeastern Alberta are located over the very large Basal Aquifer, with brackish salinity ranging from 8,000 to 24,000 ppm. Sample chemistry is included in Table 1 below. As the oil sands mines excavate new areas, Basal Aquifer brackish water is being encountered. Mine sites are either de-pressurized through bore wells or saline water is collected and ponded. Basal brackish water cannot be directly discharged due to its salinity and therefore requires desalination. Simulated and real Basal brackish water was used for the testing. It is a hard and alkaline water.

Table 1 *Analysis of sample Basal Aquifer brackish water encountered in Canadian oil sands mines*

Parameter	Quantity	Parameter	Quantity
pH	7.8	Sulfate (mg/L)	<500
Silica	5	Calcium (mg/L)	206
Bicarbonate (mg/L)*	2,120	Magnesium (mg/L)	251
Carbonate (mg/L)*	206	Sodium (mg/L)	9,100
Chloride (mg/L)	12,800	Total Dissolved Solids (TDS) (mg/L)	22,000

Reverse Osmosis on Basal Brackish Mine Water

Hardness limits RO recovery when softening or anti-scalants are not used. Reverse osmosis (RO) process modeling software, such as Dow Rosa (DOW 2012), can be used to predict the onset of fouling and maximum recovery dictated by brine chemistry. Above 10,000 ppm, the Stiff & Davis Saturation Index is the most widely used indication of calcium fouling. To limit fouling it is preferable to keep the Stiff & Davis Saturation Index below 1.8. Based on these limits, a Basal brackish RO system can achieve a maximum theoretical recovery of 50% resulting in 44,000 ppm brine. This means that 50% of inflow ends up as brine requiring further management.

The authors tested the representative Basal mine water in an RO test cell after pre-treatment with ultra filtration. Reverse osmosis (RO) was found to be effective in producing high quality permeate (<500 ppm) yet organic and inorganic fouling was a concern. In order to prevent inorganic fouling, the concentrate concentration needed to be below 45,000 ppm Total Dissolved Solids (TDS) – very similar to the result provided by the vendor supplied modeling software. Some organic fouling also resulted; however this can be addressed with pre-treatment. The species causing organic fouling were expected to be small charged organic acids.

With softening upstream of an RO unit, higher recoveries in the 75% range can be achieved. This approaches the practical osmotic pressure limit of 8% salt mass (80,000 ppm) brine but reduces brine production to 25% of inflow. Traditional softening, however, requires chemical addition and the associated handling, expense, and sludge removal. Electrochemical devices can be used to soften water without chemical addition. A similar device, pictured in Figure 2, is being tested by NASA for possible application on the International Space Station as a calcium sulfate removal device upstream of an onboard crystallizer suffering from fouling and recovery issues.

High Concentration Electrodialysis Reversal (HC-EDR) on Mine Water

Generally, an EDR unit can transport ionized molecules such as dissolved salt ions with a molecular weight less than 200 g/mol across a membrane with a maximum

80,000 ppm concentration increase. For example, transferring dissolved salts from a 500 ppm solution to an 80,000 ppm solution. A patented high concentration EDR stack (HC-EDR) can be used to broaden this concentration range by adding a third or fourth set of compartments and "bridge solutions." Salt is transported from a first exemplar concentration of 500 ppm to an 80,000 ppm transfer solution, and then to a higher concentrated 160,000 ppm brine.

The representative Basal brackish mine water was tested on the 200 L/day small-scale stack pictured in Figure 2. Data acquisition of concentrations (conductivity), temperature, electric current (ionic current), and voltage were recorded. Flow rates and pH were monitored on a twice daily basis during business hours. Data in Figure 4 shows effective desalination of the Basal brackish water, represented as the "P" solution. Salt concentrations are expressed as conductivity (mS/cm), which may be converted to salt mass using the referenced publication (Hammer 1972) or a simplified rule of thumb through multiplication by 0.67.

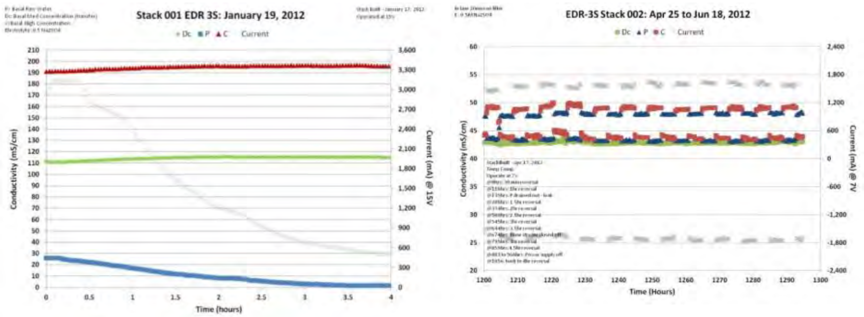


Figure 4 *HC-EDR Test Data*

The right side chart of Figure 4 shows Basal brackish desalination from a conductivity of 28 mS/cm (22,000 ppm) to below 1 mS/cm (500 ppm) and passage of the salt ions across the moderate concentration "Dc" solution and into the more highly concentrated brine "C" at 190 mS/cm (150,000 ppm). The second figure demonstrates longevity at moderate concentration: 40-50 mS/cm. A HC-EDR test cell continues to run after 1200 hours. Automatic polarity reversal is used to de-scale membranes. Results show that performance can be maintained through periodic reversal. Next steps include longevity testing at the higher 150,000 ppm concentration. Performance, flow and pressure drop measurement, and stack disassembly and autopsy revealed that the organic fouling issues encountered in the RO test cell after a matter days have not been an issue for the HC-EDR cell after almost two months of operation. This result follows industry know-how that electrodialysis is generally more resilient to organic fouling than RO due to a lack of pressurized impingement combined with ionic reversal that helps to removed lightly charged organics from the membrane surface. As a result, electrodialysis systems generally require less pretreatment than RO, do not require chemical softening upstream, and produce a lower volume brine that is often half that of RO. Brine management is generally the most expensive process step in a desalination plant. Therefore reducing brine volume through lower cost upfront methods is preferred.

Conventional Brine Management

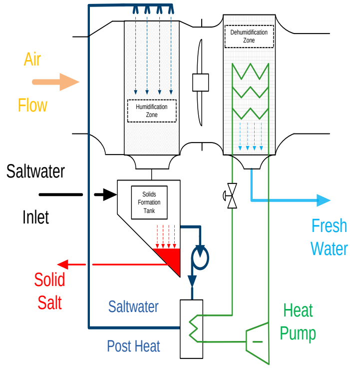
Concentrator-crystallizers are the dominant non-pond, non-deep well brine management option available today. They operate based on vapour recompression processes where saltwater is evaporated inside an alloy steel vessel, its vapour compressed in titanium built compressor, and then condensed in titanium tubes lining the alloy steel vessel. They provide the benefit of increased freshwater recovery, albeit at a historically high capital and operating cost with notable reliability concerns as a result of calcium sulfate scaling and the compressor being exposed to the saline vapour stream. The capital cost is largely due to the use of duplex alloyed steels and titanium, coupled with the need for notable site erection works. Site erection costs are being reduced through modularization. Operating costs are result of energy use and specialized personnel requirements for operation.

Humidification Dehumidification (HDH) Solids Production: the SaltMaker

The authors developed an HDH solids production system termed the "SaltMaker" as a possible alternative to concentrator-crystalizers. It produces solid salt and freshwater from a waste saltwater source in a low pressure, moderate temperature process. The electrical energy use for the SaltMaker is generally the same as concentrator-crystallizers due to the similar thermodynamic barrier (20-60 kWhe/m^3 depending on salinities and temperatures).

The SaltMaker overcomes footprint challenges of HDH systems by operating the air circuit at a higher temperatures (60-80 °C), which increases the volumetric moisture holding capacity of air by an order of magnitude over ambient operation. The patent pending heat pump drive enables heat recovery and moderate temperature operation to increase capacity. The prime mover in the system is a standard, widely available refrigerant compressor, resulting in a smaller, lower capital cost, and easier to service machine. In addition, since the heat pump cycle is closed loop on the refrigerant process, the prime mover compressor is never exposed to saline vapour, which enhances reliability.

A1.5 m^3/day pilot has been operating on seawater for over a year in Vancouver, Canada. A 25 m^3/day containerized pilot, shown in Figure 5, was dispatched to coal seam gas fields in Australia. At the time of writing a 50 m^3/day pilot was nearing completion for an Alberta oil sands project. A series of smaller 100 L/day micro-pilot systems, also pictured in Figure 5, have been developed. One such 100 L/day micro-pilot was used to further concentrate the 15% concentrated Basal brine produced by the HC-EDR. Freshwater produced had an average TDS of 200 ppm. A mixed solid salt was produced with a moisture content of 10%, resembling "wet sand." Electrical energy consumption averaged 40 kWhe/m3. Waste heat can be used to augment electrical energy consumption and reduce it to the 6-8kWhe/m3 range, however a pure electric drive was considered in this work for comparison to concentrator-crystallizers.



Containerized (left) and Micro (right) Pilot Systems

SaltMaker Process

Figure 5 *HC-EDR Test Data*

The SaltMaker consists of four subsystems described below and shown in the simplified process diagram in Figure 5.

- *Salt water system (blue):* Saltwater is pumped, heated, and sprayed into the humidification zone for evaporation of water to air. Saltwater is concentrated and cooled during the evaporation process. The more saline saltwater enters a conical vessel where solids are formed as the solution cools and becomes super-saturated. Saltwater system operating pressures and temperatures are ~100 kPa (15 psi) and 20 to 80 °C respectively. This enables the use of robust, corrosion resistant, and low cost engineered plastics such as polyvinyl chloride (PVC) and high density polyethylene (HDPE).
- *Air HDH system (orange):* Air is successively humidified by warm saltwater and dehumidified by a cool heat pump evaporator (radiator like heat exchanger evaporating refrigerant internal to the tubes). Freshwater is produced as a result of dehumidification. The air system operating pressures and temperatures are < 35kPa (5 psi) and 5-80 °C respectively.
- *Heat pump system (green):* A custom developed heat pump extracts heat from condensing water vapour in the dehumidification evaporator and upgrades it for heating the saltwater in the heat pump condenser. A standard off-the-shelf refrigerant compressor is employed.
- *Salt extraction system (red):* Solids are extracted via a screw auger, which draws salt from the base of the conical tank and dumps it into a bin.

Unique systems are used to promote precipitation and enhance de-watering.

Performance & Economic Comparison

Table 2 summarizes the results of a performance and economic comparison between three options:

- First stage RO without chemical softening followed by a second stage concentrator-crystallizer;
- First stage chemical precipitation softening and RO; second stage concentrator-crystallizer;
- First stage HC-EDR followed by a second stage SaltMaker.

Twenty year plant life, 8% interest rate, and $100/MWh electrical power were assumed. Reverse osmosis (RO) costs are based on vendor pricing; concentrator-crystallizer costs are based on general industry rules of thumb and inferred from literature adjusted for inflation (USBR 2006).

Table 2 *Comparison of performance and economics between process options. All amounts in USD.*

Performance or Economic Metric	**Option A**	**Option B**	**Option C**
First Stage			
Recovery	45%	80%	90%
Brine Discharge (ppm)	45,000	80,000	150,000
Electrical Energy (kWhe/m3)	5	5	8
Energy Cost ($/m3 S1 input)	$0.5	$0.5	$0.8
Operating Cost ($/m3 S1 input)	$0.1	$0.3	$0.1
Capital Cost ($/m3 S1 input)	$1.0	$1.5	$0.5
Sub-Total Cost ($/m3 S1 input)	**$1.6**	**$2.3**	**$1.4**
Second stage			
Inflow (% of plant input)	55%	20%	10%
Electrical Energy (kWhe/m3)	40	25	40
Energy Cost (kWhe/m3 S2 input)	$4.0	$2.5	$4.0
Operating Cost ($/m3 S2 input)	$2.0	$2.0	$1.0
Capital Cost ($/m3 S2 input)	$20.0	$20.0	$6.0
Sub-Total Cost ($/m3 S2 input)	**$26.0**	**$24.5**	**$11.0**
Energy Cost (kWhe/m3 S1 input)	$2.2	$0.5	$0.4
Operating Cost ($/m3 S1 input)	$1.1	$0.4	$0.1
Capital Cost ($/m3 S1 input)	$11.0	$4.0	$0.6
Sub-Total Cost ($/m3 S1 input)	**$14.3**	**$4.9**	**$1.1**
Total Cost ($/m3 S1 input)	**$15.9**	**$7.2**	**$2.5**

Economic calculations were levelized on a basis of cost per cubic meter treated. Total cost of ownership costs are presented on a basis of $/m3 of the first stage inlet flow, or total plant flow. The results show that option C holds the potential to reduce treatment costs ($/m3 of first stage flow) by up to one third. Option C's higher first stage recovery and in the second stage use of HDPE and PVC plastics in place of titanium and alloyed steels largely drive the potential cost advantage.

Conclusions

Reverse osmosis (RO) is an effective low cost desalination technology, especially on seawater where a convenient brine disposal means exists. Electrodialysis is generally more resilient than RO on highly fouling waters and can operate at almost double the brine concentration, resulting in half the brine volume if front-end chemical precipitation is to be avoided. A High Concentration Electrodialysis (HC-EDR) apparatus tested on Basal brackish water proved desalination and production of concentrated 15% salt mass brine. A humidification-dehumidification based SaltMaker was tested on the HC-EDR brine to reduce it to solids and freshwater at a comparable energy to concentrator-crystallizers. An economic analysis shows that the HC-EDR SaltMaker hybrid system holds the potential to reduce the cost of treatment by up to one-third. Further work is recommended. Specifically, dispatch of an integrated, automated 200 L/day HC-EDR SaltMaker pilot to a mine site to sure up in-situ performance as well as improve costing and economic analysis assumptions.

References

DOW – ROSA Software. DOW Water & Process Solutions corporate website. http://www.dowwaterandprocess.com/support_training/design_tools/rosa.htm. 2012

Hammer, W.J. and Wu,Y. 1972. Osmotic coefficients and mean activity coefficients of uni-univalent electrolytes in water at 25 °C, J. Phys. Chem. Ref. Data, Vol. 1, No. 4

USBR - US Department of the Interior, Bureau of Reclamation. Membrane Concentrate Disposal: Practices and Regulation. April 2006