

RECLAMATION

Managing Water in the West

Desalination and Water Purification Research
and Development Program Report No. 111

Zero Discharge Seawater Desalination: Integrating the Production of Freshwater, Salt, Magnesium, and Bromine

University of South Carolina
Research Foundation

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**U.S. Department of the Interior
Bureau of Reclamation
Technical Service Center
Environmental Resources Team
Water Treatment Engineering and Research Group
Denver, Colorado**

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Acronyms and Abbreviations

A	amperes
Br ₂	bromine
Ca	calcium
CaSO ₄	calcium sulfate
Cl ₂	chlorine
cm ²	square centimeters
ED	electrodialysis
CO ₂	carbon dioxide
g	gram
gpd	gallon per day
H ₂	hydrogen
HNO ₃	nitric acid
KBr	potassium bromide
kgal	kilogallon
L/sec	liters per second
kWh	kilowatthours
M	molar solution
mA/cm ²	milliamperes per square centimeters
Mg	magnesium
MgCO ₃	magnesite
mgd	million gallons per day
Mg(HCO ₃) ₂	magnesium hydrogen carbonate
Mg(OH) ₂	magnesium hydroxide
mL	milliliters
mmol/L	millimolar per liter
mS/cm	millisiemens per centimeter
MW	megawatt
Na ₂ CO ₃	sodium carbonate

Acronyms and Abbreviations (continued)

NaBr	Bromide salts
NaCl	sodium chloride
NaHSO ₃	sodium bisulfate
NaNO ₃	sodium nitrate
NaOH	sodium hydroxide
NPDES	National Pollutant Discharge Elimination System
O ₂	oxygen
ppm	parts per million
psig	pounds per square inch gauge
PVC	polyvinylchloride
RO	reverse osmosis
RTN	relative transport number
SO ₄	sulfate
SWRO	seawater reverse osmosis
TDS	total dissolved solids
V	volt
ZLD	zero liquid discharge
ZDD	zero discharge desalination
°C	degrees Centigrade
μS/cm	microsiemens per centimeter—1/1,000 of a mS/cm, used for product water conductivity. Electrical signal from ions in solution
%	percent

1. Executive Summary

As population grows, the strain on the world's freshwater supplies will increase. By 2025, about 2.7 billion people, nearly one-third of the projected population, will live in regions facing severe water scarcity according to the International Water Management Institute (Smith, 2001). Many prosperous and fast growing regions—the American Southwest, Florida, and Asia—have inadequate freshwater supplies. Nevertheless other factors such as a pleasant climate, mineral resources, job growth, and rising incomes drive growth in these regions. The needs of municipalities, industry, and citizens must be met, even as the difficulty and cost of developing new water resources increases. Desalination has become a popular option in regions where there is abundant water that is unsuitable for use due to high salinity, and there are opportunities for desalination plants that utilize thermal, electrical, or mechanical energy to recover potable water from salty solutions. The choice of desalination process type depends on many factors including salinity levels in the raw water, quantities of water needed, and the form and cost of available energy. Reverse osmosis (RO) is gaining increasing acceptance as the process of choice for desalination of seawater.

Modern RO membranes have such high salt rejection that they are capable of producing potable water (less than 500 parts per million [ppm] salinity) from seawater (nominally 35,000 ppm salinity). Furthermore, some modern RO systems are capable of achieving up to 50 percent (%) recovery of freshwater from seawater. Seawater RO plants operating at 50% recovery produce a brine waste stream having about 70,000 ppm salinity. Disposal of such brines presents significant costs and challenges for the desalination industry, which increase the time required for permits and construction of new plants and result in higher cost of water. Brine disposal to surface waters in the United States requires National Pollutant Discharge Elimination System permits, which are difficult to obtain in many areas. There are three basic ways to deal with brines from seawater desalination—discharge to the sea, deep well injection, and zero liquid discharge (ZLD) systems. A ZLD system evaporates brine leaving a salt residue for disposal or reuse. The discharge of brines back into the sea can affect the organisms in the discharge area.

This report contains the results of a study of a ZLD process for seawater reverse osmosis (SWRO) with enhanced freshwater yield and production of salable sodium chloride (NaCl), magnesium hydroxide (Mg(OH)₂), and bromine (Br₂) from the SWRO reject. The process uses electro dialysis (ED) to reduce the salinity of the reject stream from SWRO so that the salt-depleted reject stream can be recycled to the SWRO to improve the yield of freshwater. ED is already used on a large scale to recover food-grade NaCl from seawater. Indeed, there are several salt manufacturing plants in Japan that utilize ED to produce a 20% solution of NaCl brine. That brine is then evaporated to dryness with heat from the same powerplant that supplies electricity for the ED. The special ion-exchange membranes in the ED stacks are selectively permeable to Na ions

(rejecting Ca and Mg) and to Cl ions (rejecting sulfate [SO₄]) so that the recovered NaCl has considerably higher purity than salt recovered simply by evaporation of seawater or SWRO reject.

This research is based on the premise that seawater has many valuable constituents, but their value can only be realized if their separation is economically and technically feasible. There are technically feasible ways to recover many of these valuable seawater constituents (Seetharam and Srinivasan, 1978); however, the economics of the recovery are often dismal. When the concentration of a trace constituent is very low, the cost of moving the seawater through the recovery device can be greater than the value of the material recovered. If the recovery involves chemical addition, the disposal of the entire volume of chemically modified water becomes an issue.

The approach of this ZLD study is to remove in logical sequence the most accessible amounts of abundant constituents in seawater, water, and NaCl and leave remaining valuable constituents in a concentrated solution. The first step is to remove about half of the water using RO treatment. The remaining brine contains concentrated NaCl and potassium bromide [KBr], which are subsequently removed by ED. A portion of the NaCl-depleted stream is recycled to RO, and the remainder is processed for recovery of Mg(OH)₂, which is an item of commerce. NaCl in the ED brine is recovered by crystallization after concentration by evaporation. The bench-scale experiments performed in this study showed that salinity became concentrated as high as 23% in the brine produced by the ED. The NaCl content of the brine was about 10 times that of seawater, while the sulfate content was less than half that of seawater. About three-fourths of the NaCl in the brine was recovered as high-purity (greater than 99.5%) crystals. The fact that ED can concentrate the NaCl to 20% means that NaCl can be crystallized with only one-third of the thermal energy that would be required if the total amount of water in the RO reject were to be evaporated. The bromine-rich bittern that remains after NaCl recovery would be treated with chlorine (Cl₂) to oxidize Br⁻ ions to Br₂. The Br₂ would be stripped from the bittern by air, steam, or vacuum. (The steps of bromine conversion were not performed in this experimental program, but they are routinely done in the commercial production of bromine.) After recovery of the most accessible portions of water (NaCl, Br₂ and Mg(OH)₂), the residual solutions can be evaporated to dryness to produce road salt; but ultimately, minor constituents might be recovered from that residue.

All of the individual separation processes utilized in the ZLD system in this study are practiced on a commercial scale; however, in some cases, these processes were operated under conditions that were not studied previously. A mathematical model based on material and energy balances was developed for the ZLD system. Bench-scale experiments of the ZLD processes were performed in the laboratory to obtain operational data for the model. The model was used to make predictions

of the process economics. Those preliminary calculations indicated that sales of the recovered NaCl, Mg(OH)₂, and Br₂ could support the added cost of the equipment required for this ZLD process.

2. Background and Introduction

In the last half century, global demand for freshwater has doubled approximately every 15 years (Abramovitz, 1996). This growth has reached a point where today existing freshwater resources are under great stress, and it has become both more difficult and more expensive to develop new freshwater resources. One especially relevant issue is that a large proportion of the world's population (approximately 70 percent [%]) dwells in coastal zones (Konikow, 2002). Many of these coastal regions, including those in the Southeastern and Southwestern United States, rely on underground aquifers for a substantial portion of their freshwater supply. Coastal aquifers are highly sensitive to anthropogenic disturbances (Marin, 2003). In particular, if an aquifer is overdrawn, it can become contaminated by an influx of seawater and, therefore, requires desalination. So the combined effects of increasing freshwater demand and seawater intrusion into coastal aquifers are stimulating the demand for desalination.

Coastal locations on sheltered bays or near estuaries, protected wetlands, and other sensitive ecosystems are more likely to have trouble disposing of concentrated solutions that are produced when water is removed from a feed solution. Concentrate disposal problems rule out many otherwise suitable locations for industrial and municipal facilities for desalination of seawater and brackish water reverse osmosis (RO). These concentrate-disposal-constrained sites represent an important potential area for the application of zero liquid discharge (ZLD). However, the high cost of commercially available ZLD technology (e.g., brine concentrators and crystallizers) and the limitations of experimental technologies such as solar ponds and Dewvaporation have discouraged their use in treating discharge streams from desalination of both seawater and brackish water. The methods, challenges, economics, and policy implications of concentrate disposal as well as its costs have been well documented (Mickley, 1997 and 2001).

In the United States, the two States that have the biggest potential for growth of desalination capacity, Florida and California, are also States that give intense scrutiny to the impact of concentrate disposal. This scrutiny results from a combination of strict environmental regulations and a high degree of public concern about the potential for concentrate discharge to damage the ecosystems of receiving waters. The greatest environmental concern associated with brine discharge to surface water relates to the potential harm that concentrate disposal may pose to bottom-dwelling organisms located in the discharge area. Following the guideline that a 1,000-part-per-million (ppm) change in the salinity can be tolerated by most organisms, the volume of 70,000-ppm brine from a seawater reverse osmosis (SWRO) plant would require dilution with 35 volumes of seawater. In some cases, that dilution can be achieved by combining the brine with another outflow such as cooling water from a powerplant; otherwise, an underwater structure is needed to disperse the brine. Such underwater structures are disruptive to the sea bottom, require inspection and maintenance, and are

subject to damage by fishing nets, anchors, or natural movements at the sea bottom. The cost of brine disposal to the sea will vary widely depending upon site-specific circumstances. The cost of pipelines into the deep ocean, where the effects are more likely to be negligible, increase exponentially with depth. The capital cost of Tampa Bay Number 2 desalination plant per cubic meter of product is estimated at \$4,587 for long-distance brine disposal versus \$3,057 for near-shore disposal (Desalination Tracker, 2003).

Concentrate disposal imposes significant costs and permitting requirements:

- ◆ Direct disposal costs, such as injection wells, pipelines, water quality sampling, instream biodiversity studies, can represent between 10 and 50% of the total cost of freshwater production (Mickley, private correspondence).
- ◆ Time and expense required to obtain discharge permits can be substantial. For the 25-million-gallon-per-day SWRO plant in Tampa, Florida, it took 12 months to obtain the National Pollutant Discharge Elimination System (NPDES) permit for brine disposal to the sea. Approvals from eight different State agencies were required, and the developer had to agree to conduct extensive long-term monitoring of receiving waters. Siting on Tampa Bay was feasible only because the concentrate will be diluted by a factor of 70 before it is discharged into Tampa Bay. The plan calls for concentrate to be mixed with cooling water from the neighboring 1,825-megawatt (MW) Big Bend power station.

Deep well disposal is often used for hazardous wastes, and it has been used for desalination brines in Florida. Published estimates of capital costs are approximately \$1 per gallon per day (gpd) of desalination capacity. The applicability of deep well injection for large desalination plants is questionable because of the sheer volume of the brine and the possibility of contamination of ground water.

ZLD systems are widely used in other industries situations where liquid wastes cannot be discharged. These systems usually include evaporative brine concentration followed by crystallization or spray drying to recover solids. Common ZLD processes include the thermal brine concentrator and crystallizer (manufactured by Ionics-RCC and Aquatech). This technology can be used to separate SWRO concentrate into freshwater and dry salt. However, the capital costs and electrical consumption, approximately \$6,000- \$9,000 per cubic meter of daily capacity (\$23-\$34 per gpd and approximately 30 kilowatthours (kWh) per cubic meter) of freshwater produced, is so high that it has not been used to achieve “zero discharge” SWRO. Water removal from dilute brines is usually accomplished by vapor compression or high-efficiency, multiple-effect evaporators. The vapor then condenses in the heat exchanger that contacts the brine to form potable water with less than 10 ppm of total dissolved solids (TDS). Heat for evaporating water from saturated brines is usually provided by steam. Even with the efficiencies of vapor compression, the capital and operating costs of existing ZLD processes are substantial. The ZLD process of this study shares

some similarities to the Ionics RCC Brine Concentrator, but that process lacks the capability of isolating the salts so that individual salts can be recovered and sold as high-value products.

A ZLD process with no chemical recovery was installed at the 665-MW Doswell Combined Cycle Facility in Virginia to treat this liquid waste, including RO reject and mixed-bed regenerate waste from a makeup demineralizer. The ZLD process includes preconcentration of feedwater by electrodialysis reversal, a step that saved \$900,000 in capital and \$682 per day in operating cost compared to evaporation without preconcentration (Seigworth et al., 1995).

Evaporation ponds can also be characterized as part of a ZLD process; but they are not broadly applicable, because they require unique climatic conditions and a large area of land.

3. The New ZDD Process

The concept that was investigated in this study is called Zero Discharge Desalination (ZDD). ZDD is similar to a zero liquid discharge (ZLD) system but differs from the ZLD mentioned above in that it specifically targets desalination and includes the separation of the salts into salable products. The ZDD concept utilizes the energy-saving feature of electro dialysis (ED) to remove the monovalent salts (primarily NaCl and potassium bromide [KBr]) from the RO reject and concentrate them about threefold before the evaporation step. A simplified version of the ZDD concept is illustrated in figure 1. The seawater is pretreated to remove particulate matter and objectionable ions. (Pretreatment was not within the scope of this study, but results indicated the need for removal of Calcium (Ca) at the beginning of the process.) The pretreated seawater passes through the RO where about half of the water is removed as permeate.

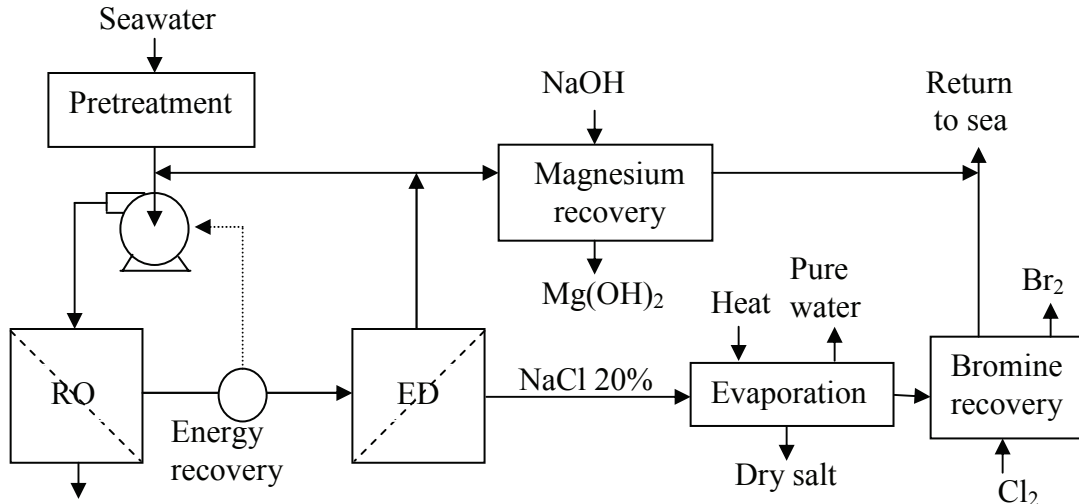


Figure 1. Process Schematic for Zero Discharge Desalination with Optional Seawater Discharge.

The reject stream from the RO, having about twice the ionic concentrations of seawater, is fed to the ED stack, which produces a concentrate stream with about 20% dissolved salts (primarily NaCl) and a diluate stream with about the same salinity as seawater. The ED can be fine-tuned to produce a diluate with the same density as seawater so that the diluate can be returned to the sea without provisions for mixing. (For a true zero discharge process, a portion of the ED diluate would be processed for magnesium (Mg) recovery and then evaporated to dryness, and the remainder would be recycled to the RO feed as shown in figure 2.)

The ED stack contains special ion-exchange membranes that are selective to the transport of monovalent ions, in contrast to conventional membrane that

selectively transport divalent ions. The predominant monovalent ions and their relative transport through the special membranes are Na^+ : 1, K^+ : 0.8, Cl^- : 1, Br^- : 3.8 and HCO_3^- : 0.5. The predominant divalent ions and their relative transport through the special membranes are Mg^{++} : 0.05, Ca^{++} : 0.11, and SO_4^{--} : 0.03. Because of the strong rejection of divalent ions, the 20+ percent (%) brine produced by ED has considerably higher NaCl purity than brine produced by RO. Evaporation of the ED brine precipitates high-purity NaCl that can be processed and sold for commercial use. The potential value of the NaCl suggests that this portion of the ZDD process should be designed to maximize the quality and quantity of the NaCl product.

Most of the bromide from the seawater is concentrated in the ED brine and can subsequently be recovered from the bittern that remains after the NaCl is precipitated. The reasons for this movement of bromide are as follows:

1. Bromide ions are rejected by RO membranes.
2. The RO reject is treated by ED where the Br^- (along with NaCl) becomes further concentrated. The anion-exchange membranes used in ED for salt recovery have Br/Cl selectivity of about 4/1; this will be discussed further later.
3. Bromide salts (NaBr) are substantially more soluble than chloride salts (NaCl). Therefore, sequential evaporation of the ED brine precipitates the NaCl first and leaves a bittern with highly concentrated Br^- ions that have the potential to be converted to Br_2 and recovered for sale.

For simplicity, the processes of $\text{Br}^- \rightarrow \text{Br}_2$ conversion and Br_2 recovery are shown in figure 1 as a single operation. In reality, those steps are more complex and require separate pieces of equipment for contacting the bromide-rich bittern with Cl_2 made by electrolysis, air-stripping, or steaming out the Br_2 and residual Cl_2 , condensation or absorption of Br_2 from the strip stream, and purification of the Br_2 by distillation. Analysis of the cost of Br_2 production was beyond the scope of this study. A less capital-intensive approach would be to recover crude bromide salts from the bittern and sell them as a raw material to a chemical company (e.g., Albemarle or Great Lakes Chemicals) that processes bromine.

A portion of the NaCl-depleted ED diluate (refer to figure 1) is combined with seawater and recycled to the primary RO system. Even though ED is capable of reducing the salinity of the diluate down to the salinity of seawater, the entire diluate stream cannot be recycled due to its increased content of sparingly soluble salts, particularly calcium sulfate (CaSO_4). If the remainder of the ED diluate cannot be returned to the sea, it can be evaporated to recover additional water and road salt as shown in figure 2. Energy recovery turbines would be used in the pressure letdown for the RO reject to recover a portion of the energy and transmit it to the RO feed pump.

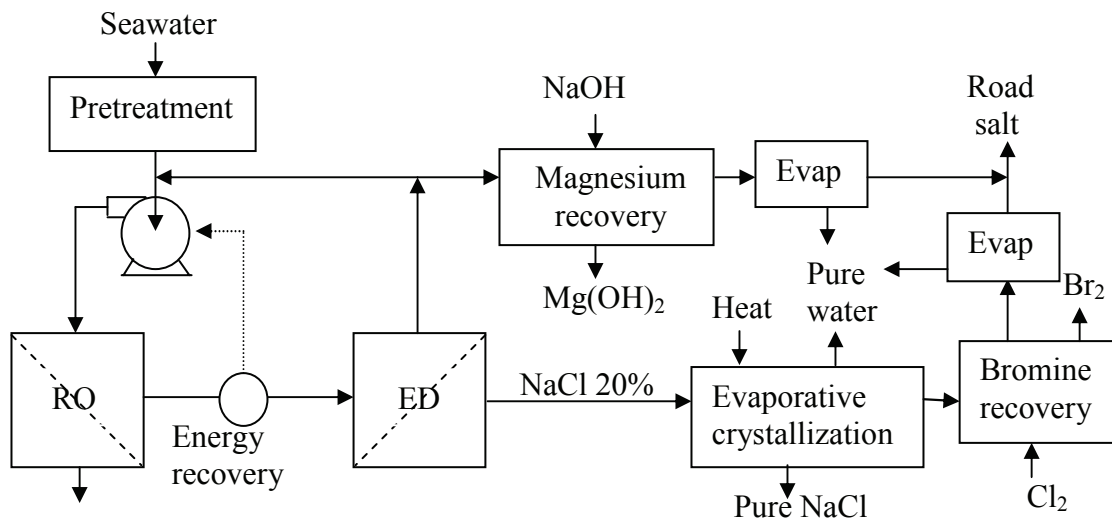


Figure 2. Process Schematic for Zero Discharge Desalination.

The Mg ion concentration in the ED diluate is about 5 five times greater than the Mg ion concentration in seawater if the diluate is recycled to the RO and about two times greater without recycle. This high concentration allows for more efficient Mg recovery in the proposed process as compared to Mg recovered in plants supplied with seawater. The Mg is precipitated by the addition of sodium hydroxide (NaOH) that is purchased or made on-site by electrolysis of NaCl brine. The brine for electrolysis can be either from the NaCl crystal product or directly from the ED after purification to remove trace divalent ions.

Cl₂ produced in the electrolysis cell can be used for the production of Br₂. Since the Br content of seawater is much lower than the Mg content, there would be excess chlorine (Cl₂) available for sale or for use to chlorinate water produced in the plant. The use of Cl₂ produced onsite would eliminate the need to purchase and store liquid Cl₂, which is a hazardous substance.

Japan has used ED to recover NaCl from seawater to produce edible salt on a large scale for about 40 years. In recent years, ED plants have been installed by Japanese companies in Kuwait and South Korea to recover NaCl from seawater to use in chlor-alkali plants. The idea of combining RO and ED to produce freshwater and NaCl has been studied by others (Hayashi, 2000), but there appear to be no serious studies to recover the more valuable solutes, Mg and Br. The benefit of recovering NaCl from RO concentrate is that the starting salt concentration is twice that of seawater. It has been reported that the energy consumption of salt manufacture with SWRO reject as the feed is 80% of that with seawater as the feed (Tanaka et al., 2003).

Although it has higher capital cost than stand-alone RO technology, the ZDD technology could potentially reduce the cost of seawater desalination when all the costs and benefits are considered. ZDD also has the potential to become less expensive than ZLD technology for seawater desalination. The combination of the two aspects in one package should increase the market for seawater

desalination to locations where it might not otherwise be possible due to disposal/environmental challenges.

If the proposed system performs as projected, it will have the following advantages:

- ◆ It will allow for RO plants to be built in locations (sheltered bays, sites near estuaries, protected wetlands, and breeding grounds for protected species) where a plant might not otherwise be built due to the inability to obtain an NPDES permit.
- ◆ By not requiring an NPDES permit, it will reduce the time and expense involved in building new RO plants.
- ◆ It will reduce the costs associated with concentrate disposal and, therefore, reduce the total cost of freshwater production.

4. Work Performed and Results

4.1 Task 1 – Design and Assemble Lab-Scale RO-ED System

The lab-scale system was designed around a Filmtec SW30-2514 RO module (rated at 100 gpd) that was part of an Aqua Whisper 170 Watermaker by Sea Recovery. A 0.5-gpm positive displacement pump by CAT was used to supply the RO with high-pressure feed from a 30-gallon polyethylene tank. Reject flowed through a backpressure valve and back into the tank. RO permeate could be either returned to the tank for steady-state operation or diverted to collection buckets when the system was being used to concentrate salt. The ED system was also fed from the same tank. A refrigeration coil in the tank was used to dissipate heat that built up from the circulation of the RO reject. It was possible to operate the ED and RO simultaneously, but that mode of operation caused the solution in the tank to become too warm, even when the refrigeration coil was used.

The ED stack was a Model TS-2 (Tokuyama Corp.) with 10 cell pairs of Neosepta CMS and ACS univalent-selective ion-exchange membranes (Tokuyama Corp.). Each membrane had 200 square centimeters (cm^2) of area exposed to electric current flow. The power supply for the ED was set to deliver a constant current of 8 amperes (A) according to the membrane manufacturer's recommendation for a maximum current density of 40 milliamperes per square centimeters (mA/cm^2). The ED system had three flowing streams—diluate, concentrate, and electrode rinse—that were circulated through the stack with magnetic-drive pumps (Iwaki Model MD-15R). The reservoir for the electrode rinse was a 3-liter, windowed, polyvinylchloride (PVC) tank. The sodium nitrate (NaNO_3) electrode rinse solutions returning from the anode and cathode flowed to two sides of a common tank divided by a baffle to prevent mixing of the oxygen (O_2) and hydrogen (H_2) generated at the electrodes.

The concentrate reservoir was a section of PVC pipe with an overflow that could be collected or diverted to the feed tank. The holdup volume in the concentrate loop was 200 milliliters (mL), barely enough to keep the solution line filled when the pump was started. Minimization of concentrate volume was important to ensure that the measured conductivity of the concentrate stream represented what was being produced at that moment by the ED stack. (It should be noted here that the ions migrating through the ED membranes drag along water of hydration, roughly 5 to 10 water molecules for each ion, so the volume of the concentrate loop increases at a rate proportional to the flow of electric current through the membranes.) The concentrate loop was set up so that the volume being produced was removed continuously from the circulation loop. Concentrate was removed via a peristaltic pump that was adjusted to pump at a rate slightly higher than the rate of concentrate production. A small amount of air was pumped when the liquid level dropped below the suction tube of the pump.

Instrumentation for the system included toroidal conductivity sensors inserted into tees in the solution lines of the ED diluate and concentrate lines and in the feed tank. The tee for the conductivity sensor for the ED concentrate was modified by filling void space with silicone room temperature vulcanizing rubber so that all of the concentrate solution flowed through the hole in the sensor. Sensors for RO reject pressure and for current and voltage to the ED stack were also used. All sensors were connected to a signal processor that was monitored by a program written in Lab View (National Instruments). Data from the sensors were recorded every 10 seconds, averaged with values from the previous six measurements to avoid effects of noise, displayed on a computer monitor, and stored on a spreadsheet.

4.2 Task 2 – Operate the Lab-Scale RO-ED System with NaCl Feed

Shakedown testing of the RO-ED system was accomplished with a synthetic feed solution of NaCl in tap water. Using this feed that was free of potential fouling materials allowed more flexibility in the initial testing. Concentrations of the solutions were determined by measurement of electrical conductivity and multiplication of those values by calculated values of the equivalent conductance of NaCl solutions obtained from published data. Experimental data from the operations with NaCl feed allowed baseline values to be established for operating parameters so that deviations from those baseline data would be recognized and quantified during the experiments with seawater. During the shakedown, testing procedures were developed to manage the return of portions of the output solutions to the feed tank in order to simulate steady-state conditions with various percentages of permeate recovery in a large-scale system. The RO and ED were fed from the same 50-gallon tank, and the RO reject and ED diluate were continuously returned to the feed tank. Since the capacity of the RO was greater than that of the ED, returning a portion of the RO permeate to the feed tank prevented the buildup of salinity in the feed tank.

4.2.1 Operating Conditions with NaCl Feed Solution

- Initial feed solution conductivity: 60 millisiemens per centimeter (mS/cm)
- RO pressure: 908 pounds per square inch gauge (psig)
- Feed tank temperature: 25 degrees Centigrade (°C)
- RO permeate conductivity: 0.292 mS/cm
- RO reject conductivity at end of batch: 57 mS/cm
- ED concentrate conductivity at beginning of batch: 190 mS/cm
- ED concentrate conductivity at end of batch: 200 mS/cm
- ED stack (10 cells + electrodes) voltage: 10.7 volts (V)
- ED current: 8.5 A

4.3 Task 3 – Operate the Lab-Scale RO-ED System with Seawater Feed

Seawater for the experiments was collected in 5-gallon pails from the Atlantic Ocean near Hilton Head, South Carolina. The contents of the pails were injected with 10 mL of Clorox prior to sealing and then treated with sodium bisulfate (NaHSO_3) to neutralize the Cl_2 prior to being poured into the feed tank. In a typical experiment, the feed tank was filled with seawater, and the RO was operated first with the diluate returned to the feed tank until steady state was observed. Then the RO permeate was diverted to collection pails, and RO operation was continued until the RO reject salinity had doubled, as indicated by temperature-corrected conductivity measurements. Then, additional pails of seawater were added to the feed tank, and the RO treatment was continued until the tank was nearly full of RO reject with double the salinity of seawater, after which the RO experiment was terminated.

The RO reject in the feed tank was treated with ED to remove salt from the solution. First, the concentrate stream from the ED stack was returned to the feed tank until steady state conditions of temperature, current, voltage, and conductivity were observed. Then, the overflow from the ED concentrate loop was diverted to a graduated cylinder.

4.3.1 Operating Conditions for RO Treatment of Seawater

- ◆ Conditions at beginning of experiment:
 - Feed solution conductivity: 44 mS/cm
 - RO pressure: 887 psig
 - Feed tank temperature: 21 °C
 - RO permeate conductivity: 0.238 mS/cm
- ◆ Conditions at end of experiment:
 - Reject solution conductivity: 73 mS/cm
 - RO pressure: 1,005 psig
 - Feed tank temperature: 22 °C
 - RO permeate conductivity: 0.536 mS/cm

4.3.2 Operating Conditions for ED Treatment of Seawater RO Reject

- ◆ Conditions at beginning of experiment:
 - Feed solution conductivity: 75.5 mS/cm
 - ED brine conductivity: 200 mS/cm
 - ED stack (10 cells + electrodes) voltage: 14.8 V
 - ED current: 7.9 A
 - Temperature: 22 °C

- ◆ Conditions at point of maximum brine conductivity:
 - Feed solution conductivity: 67.9 mS/cm
 - ED brine conductivity: 212.5 mS/cm
 - ED stack (10 cells + electrodes) voltage: 14.0 V
 - ED current: 8.0 A
 - Temperature: 25 °C
- ◆ Conditions at end of experiment:
 - Feed solution conductivity: 42.9 mS/cm
 - ED brine conductivity: 204 mS/cm
 - ED stack (10 cells + electrodes) voltage: 19.2 V
 - ED current: 7.4 A
 - Temperature: 24 °C

4.4 Task 4 – Perform Mg(OH)₂ Precipitations

The diluate from the electrodialysis treatment of seawater RO reject (3,100 ppm of Mg and 760 ppm of Ca) was pretreated to remove Ca. Addition of 0.25 mL of 1 molar solution (M) NaOH brought the pH from 8.26 to 9.5. The addition of 1 gram (g) of sodium carbonate (Na₂CO₃) powder in small increments produced a precipitate and raised the pH to 9.9. The precipitate was recovered on a porous Teflon filter, dissolved in HNO₃, and analyzed for Mg and Ca. The concentrations in the solution prepared by dissolution of the precipitate were 5,500 ppm of Mg and 3,300 ppm of Ca. A small amount of secondary precipitate was observed in the first filtrate. Filtration, dissolution of the secondary precipitate and analysis showed 180 ppm of Mg and 32 ppm of Ca. The second filtrate contained 1,300 ppm of Mg and 10 ppm of Ca. These results indicated that adding Na₂CO₃ is effective for removing most of the Ca, but progressively larger amounts of Mg are co-precipitated in attempts to remove the last traces of Ca.

Another 50 mL was titrated to pH 9.5 with NaOH and then 10.2 mL of an aqueous solution of Na₂CO₃ (9.265 %) was added incrementally. The final pH was 9.87. The precipitate was filtered and dissolved with nitric acid (HNO₃), and analysis showed 5,900 ppm of Mg and 2,900 ppm of Ca. The filtrate had 870 ppm of Mg and 12 ppm of Ca. Addition of 42.5 mL of 1 M NaOH raised the pH to 11.83 and produced a precipitate that was removed by filtration and dissolved. Analysis of the dissolved precipitate showed 5,000 ppm of Mg and 44 ppm of Ca.

These results indicate that pretreatment with Na₂CO₃ to remove Ca can produce a brine that yields Mg(OH)₂ having greater than 99% purity. The laboratory experiments revealed no advantage to using liquid rather than solid Na₂CO₃ for the precipitation of CaCO₃. The large amount of Mg that co-precipitated with the Ca is of concern for several reasons.

- ◆ Mg precipitated by Na₂CO₃ is not available for recovery.

- ◆ The precipitation of Mg increases the amount of Na_2CO_3 needed for Ca removal.
- ◆ The additional volume of precipitate increases cost of disposal or further processing.

The amount of Na_2CO_3 used was about 10 times the stoichiometric amount required for Ca, while about half of the Mg was co-precipitated with the Ca. It is likely that a lesser amount of Na_2CO_3 would have decreased the purity of the $\text{Mg}(\text{OH})_2$ in the brine; but further study is required to determine the optimum amount of Na_2CO_3 needed to strike a balance of product purity, Mg yield, and chemical cost. The Mg precipitated by Na_2CO_3 could potentially be separated and recovered from the precipitate by adding carbon dioxide (CO_2) under pressure to form highly soluble magnesium hydrogen carbonate ($\text{Mg}(\text{HCO}_3)_2$). Such a technique was used during the mid-19th century to prepare pure Mg compounds from calcined dolomite (Pattison, 1841). Adding CO_2 to the slurry of Ca and Mg carbonates will produce a concentrated solution of $\text{Mg}(\text{HCO}_3)_2$ in carbonic acid. After filtration to remove CaCO_3 , the solution will yield solid magnesite (MgCO_3) when the CO_2 pressure is released. The recovered CO_2 can be recovered and reused to reduce the overall cost of this process.

4.5 Task 5 – Perform Salt Crystallizations in Laboratory Evaporator

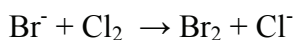
The primary purpose of this task was to obtain samples of salt and bittern for chemical analyses. The experiments were performed in laboratory glassware and provided no direct information about energy consumption or fouling of heat-transfer surfaces. The apparatus consisted of a 1-liter, round-bottom flask fitted with a glass thermometer and within an electrically heated sand bath atop a magnetic stirrer. This apparatus, along with a glass condenser cooled by tap water, were both mounted on a ring stand. The ring stand sat on the platform of an electronic balance so that the weight loss could be monitored continuously. Half-liter batches of ED concentrate solution from the ED (23% TDS) were heated in a stirred flask, and the water vapor was collected in a water-cooled condenser.

Three cuts of salt crystals were collected on a Buchner filter, rinsed with some of the collected condensate, and dried in an oven; the rinse water was returned to the evaporator. Samples of the salt crystals were submitted for chemical analysis to determine how much of the collected salt would meet the 99.5% NaCl purity specification for Vacuum Pan Evaporated Salt. Vacuum Pan refers to salt that is made from purified brine from which the water is removed in vapor-compression or multiple-effect evaporators. The weights and Na^+ -cation purities of salt crystals collected in the three batches were 52 g: 99.95%; 53 g: 99.48%; and 24g: 97.35%. Analysis of the brine and bittern showed an eightfold increase in Mg concentration and no increase in Cl concentration, which indicates an

eightfold reduction in solution volume as NaCl crystallizes. Based on these measurements, about 87% of the NaCl in the ED concentrate was crystallized. About 80% of the recovered NaCl meets the 99.5% purity specification for Vacuum Pan Evaporated Salt. The remaining 20% is still of higher quality than road salt.

4.6 Task 6 – Study Options for Bromine Product

Br⁻ ions in the bittern are present in concentrations about 30 times greater than in seawater, which should be attractive for recovery. The current conventional process for bromine recovery as Br₂ utilizes Cl₂ to oxidize Br⁻ ions by the reaction:



The Br₂ is then stripped from the bittern with air or steam. Air stripping is generally more economical at seawater concentrations of bromine to avoid the high energy cost of heating the large mass of water, but steam stripping would be preferred for the higher concentrations expected for this process. The vapor from the steam stripping is condensed to form a two-phase liquid. The aqueous phase containing about 3% of Br₂ is recycled to the stripper, and the Br₂ phase is purified by distillation to remove residual water and Cl₂, which are returned to the process.

The process model described under Task 7 indicated that about 0.38 tons of Br⁻ ion would be recovered in the ED brine associated with 1 million gallons of seawater RO permeate, and essentially all of that could be recovered as Br₂ by conventional techniques from the bittern after NaCl crystallization. Alternative means of recovering Br₂ have been investigated by others. Qi and Cussler (1985) reported that Br₂ generated by chlorination brine could be recovered through a hydrophobic, microporous membrane (they used Celgard). With this approach, the Br₂ recovery process could be compact with a small footprint. Yalcin et al. (1997) reported the formation of Br₂ by direct electrolysis of Br-rich bittern from evaporation ponds used for salt production. The Br₂ was formed as a liquid on a graphite anode and fell to the bottom of the cell where it could be recovered as a liquid. The cell potential was maintained below 1.99 V, a value sufficient to discharge Br₂ but insufficient to discharge Cl₂. There is some H₂ produced at the cathode of the electrolytic cell as well as in the ED, but the quantity of H₂ would be insufficient for economical recovery.

4.7 Task 7 – Prepare a Mathematical Model of the Entire ZDD Process

The task of modeling the RO/ED system involved preparing mathematical equations to describe and predict the flow rates and ionic compositions of the

process streams as shown in figure 1. The ionic composition of each process stream was modeled to contain four cations (Na^+ , K^+ , Mg^{++} , and Ca^{++}) and four anions (Cl^- , SO_4^- , Br^- , and HCO_3^-). The concentrations of these ions in seawater were based on average values listed in the *CRC Handbook*, 24th Edition. The amount of the next most abundant cation, Sr^{++} , was lumped with the Ca^{++} concentration, because they have similar properties. The value for the concentration of HCO_3^- was treated as a variable to balance the positive and negative ionic charges in the seawater. Since the mass balance equations for each of the individual processes included a charge-balancing equation, this initial adjustment of HCO_3^- concentration sufficed for all of the processes.

The equations for modeling the RO process included an expression for membrane permeability to cations relative to Na^+ and permeability of anions relative to Cl^- . Thus, there were six parameters for RO membrane permeability that needed to be evaluated based on analysis of samples from process streams during operation of the RO unit. Preliminary values of these permeability parameters were estimated on the basis of data provided by the membrane manufacturers.

For the ED process, the parameter known as “relative transport number” (RTN) was employed in the calculation of the fluxes of the various ions through the membranes. RTN for Mg^{++} compared to Na^+ is defined as:

$$\text{RTN}_{\text{Mg}/\text{Na}} = (\tau_{\text{Mg}}/\tau_{\text{Na}})/(C_{\text{Mg}}/C_{\text{Na}})$$

where τ is the fraction of the electric current carried by the designated cation, and C is the concentration of that ion in the diluate solution.

In practice, the ED process will be operated with no feed to the concentrating stream, so all of the ions in the ED concentrate stream will be present in concentrations proportional to their transport numbers through the membranes, i.e. $[\text{Mg}^{++}]/[\text{Na}^+]_{\text{conc}} = (\tau_{\text{Mg}}/\tau_{\text{Na}})$. Therefore, the RTN values for each ion can be calculated from the experimental values of the concentrations in the diluate and concentrate streams. For example,

$$\text{RTN}_{\text{Mg}/\text{Na}} = [\text{Mg}^{++}]/[\text{Na}^+]_{\text{conc}} / [\text{Mg}^{++}]/[\text{Na}^+]_{\text{dil.}}$$

Since RO is characterized by substantial increases in the concentration of ions in the reject stream but minor changes in the relative concentrations of ions, it seemed reasonable to model the RO process as a single stage of treatment. In contrast, the ED process utilizes membranes with substantial selectivity between monovalent and divalent anions and cations. To deal with the resulting changes in relative concentrations of ions in the diluate, the model of the ED process was divided into nine stages. The diluate from one stage became the feed for the next stage. The concentrate from each stage was collected and blended with the concentrate from other ED stages to make a composite ED concentrate.

The mathematical model for the entire system was based on equations for the individual processes that were solved algebraically. Each process was treated

individually to facilitate alteration of the sequence of the processes. In the model for the RO process, there are 27 unknowns (dependent variables) (i.e., 8 concentrations and 1 flow rate for each of the 3 streams (feed, permeate, and reject). The 27 equations needed to complete the model for the RO include: 8 material balances for the ions, 6 equations utilizing relative permeability, 1 overall balance of flow rates, 1 balance of anion and cation charges, and 8 equations for the concentrations of the ions in the RO feed. That feed stream is a blend of seawater and a recycled process stream from the ED diluate. The remaining three equations are: (1) defining salt concentration of the permeate, (2) defining the percent of RO feed recovered as permeate, and (3) defining the rate of permeate production.

The model for each stage of the ED process also has 27 dependent variables. Of the 27 required equations, the first 24 are analogous to the RO process. The remaining three equations are: (1) defining ED concentrate salinity, (2) defining Na^+ in each ED stage, and (3) equating the ED feed rate to the RO reject flow rate or the diluate rate from the previous ED stage. Heat balances and energy inputs to the individual processes were also included in the model. Calculations were done on a computer spreadsheet.

Simulation of the crystallization of NaCl was accomplished by an iterative process whereby the concentrations of the ions were increased by a factor of 1.25 for each iteration. Solubility of NaCl was determined by an empirical equation for its solubility parameter based on data reported for seawater evaporation ponds (Zhou and Li, 1995). Iterations continued until the concentration of Na^+ ions began to drop precipitously.

4.8 Task 8 – Calibrate the Process Model with Experimental Data from the Lab-Scale RO-ED Apparatus

Samples of the process streams from the seawater experiments were analyzed by atomic absorption (for cations) and ion chromatography (for anions). No attempt was made to analyze for bicarbonate, because the potential for changes due to contact with air would have made the results meaningless. The relative concentrations of ions in the brine and the diluate from the ED were used to estimate the relative transport numbers of the ions through the ion-exchange membranes in the ED stack. The RTN of Mg^{++} ions compared to Na^+ ions was determined by the expression

$$\text{RTN}_{\text{Mg/Na}} = ([\text{Mg}^{++}]/[\text{Na}^+]_{\text{brine}}) / ([\text{Mg}^{++}]/[\text{Na}^+]_{\text{diluate}})$$

Similar equations apply to the transport of other cations relative to Na^+ and other anions relative to Cl^- . The relative transport numbers calculated from these analytical data are Na^+ : 1, K^+ : 0.8, Mg^{++} : 0.05, Ca^{++} : 0.11, Cl^- : 1, Br^- : 3.8, and SO_4^{--} : 0.03. These values were used in the spreadsheet to calculate mass balances for various scenarios.

The calibrated model was used to calculate operating parameters and economics for utilization of the idle SWRO plant at Santa Barbara, California. That plant has RO equipment that would produce 3,000 acre-feet of potable water annually. The RO permeate would be 3 million gallons per day (mgd) (130 liters per second [L/sec]) if the plant were online 90% of the time. Calculations were made for the process depicted in figure 3 (which is similar to figure 1). ED is used to recover NaCl from the RO reject, after which half of the ED diluate is recycled. The other half of the ED diluate is mixed with the bittern (i.e., the small volume of saturated solution that remains after evaporative crystallization for recovery of NaCl).

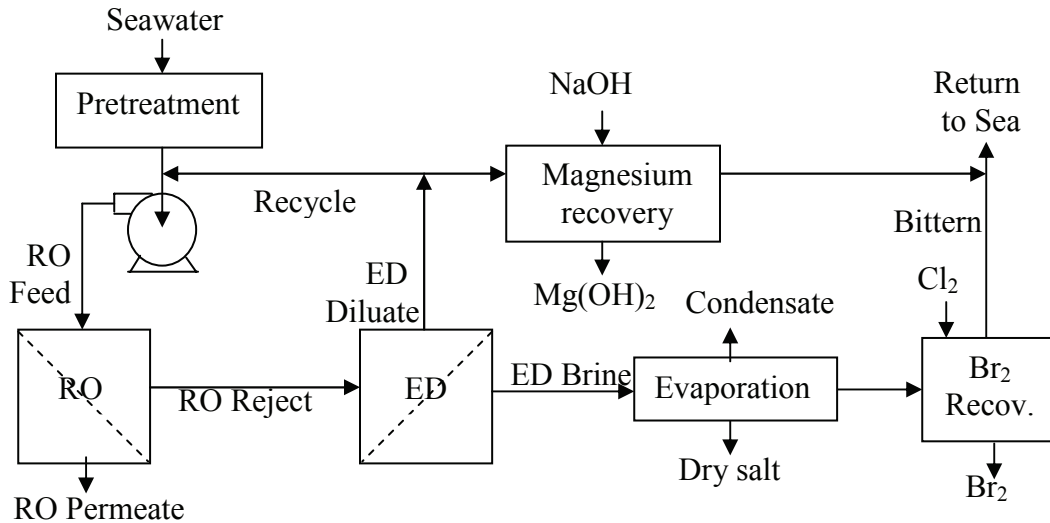


Figure 3. Flow Schematic of Scenario Used for Calculations with Calibrated Model.

Table 1 shows the mass balance calculated with the calibrated model for a scenario in which only sand filtration is used for RO pretreatment. Water recovery for this scenario is 76%. The value in the last row and column of table 1, the density of the mixture comprising half of the ED diluate (after precipitation of $Mg(OH)_2$ with NaOH) and all of the Br_2 -depleted bittern, is slightly higher than the density of seawater.

The density issue was addressed in the scenario shown in table 2 where the incoming seawater was partially softened by the addition of $Ca(OH)_2$ to precipitate the calcium associated with alkalinity and the addition of Na_2CO_3 to precipitate 75% of the Ca^{++} remaining after lime softening. A small amount of $MgCO_3$ was precipitated from the seawater along with the $CaCO_3$, so the amount of magnesium available for profitable recovery is reduced slightly. The partial softening allowed a higher level of NaCl removal by the ED and a larger portion of the NaCl to be crystallized. A major advantage of this scenario is that the density of the combined ED diluate and bittern streams is about the same as the density of seawater, so the discharge of this combined stream to the sea should be

Table 1. Material Balance with Sand Filtration of Seawater, Half of ED Diluate Recycled to RO Feed, Mg(OH)₂ Precipitation with NaOH, Br₂ Recovery, and Discharge of Effluent to the Sea

Stream	Flow	Ionic Composition (millimolar)								Density
	L/sec	Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Cl ⁻	Br ⁻	SO ₄ ⁼	HCO ₃ ⁻	kg/L
Seawater	207	459	9.72	52.3	9.98	535	0.87	27.6	2.31	1.024
RO Feed	260	379	8.26	74.9	12.9	476	0.69	42.2	2.40	1.023
RO Permeate	130	7.08	0.15	0.56	0.097	8.31	0.012	0.074	0.084	0.998
RO Reject	130	751	16.37	149	25.8	943	1.38	84	4.71	1.046
ED Diluate	105	64	2.53	164	24.5	241	0	100	2.75	1.015
Recycle	53	64	2.53	164	24.5	241	0	100	2.75	1.015
Mg Recov. Outlet	53	391	2.53	1	22.2	241	0	100	0.40	1.017
ED Brine	25	3,700	75.8	86.9	31.1	3,960	7.28	18.8	13.2	1.173
Condensate	0	0	0.0	0.0	0.0	0	0	0.0	0.0	0.998
Bittern	4.1	2,060	452	518	185	3,570	43.4	112.3	78.4	1.161
Br Recov. Outlet	4.1	2,060	452	518	185	3,610	2.2	112.3	78.4	1.175
Discharge to Sea	57	512	35	38	34	485	0.16	100	6	1.027

Table 2. Material Balance with Partial Seawater Softening, 60% of ED Diluate Recycled to RO Feed, Mg(OH)₂ Precipitation with NaOH, Br₂ Recovery, and Discharge of Density-Balanced Effluent to the Sea

Stream	Flow	Ionic Composition (millimolar)								Density
	L/sec	Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Cl ⁻	Br ⁻	SO ₄ ⁼	HCO ₃ ⁻	kg/L
Seawater	195	459	9.72	52.3	9.98	535	0.87	27.6	2.31	1.024
RO Feed	260	371	7.75	79.6	2.7	442	0.65	49.9	0.30	1.022
RO Permeate	130	7.13	0.15	0.61	0.021	8.34	0.012	0.094	0.011	0.998
RO Reject	130	734	15.36	159	5.4	877	1.29	100	0.58	1.045
ED Diluate	108	45	1.85	168	4.9	164	0	114	0.29	1.012
Recycle	65	45	1.85	168	4.9	164	0	114	0.29	1.012
Mg Recov. Outlet	43	378	1.85	1	5.0	164	0	114	0.40	1.015
ED Brine	22	4,170	82.6	113.7	8.0	4,430	7.73	29.2	2.0	1.183
Condensate	0	0	0.0	0.0	0.0	0	0	0.0	0.0	0.998
Bittern	2.9	1,390	614	845	59	3,310	57.5	217.0	15.2	1.150
Br Recov. Outlet	2.9	1,390	614	845	59	3,360	2.9	217.0	15.2	1.163
Discharge to Sea	46	442	41	54	8	366	0.18	120	1	1.024

combined effects of condensate collection and ED-diluate utilization boost the overall recovery for the system to 79% of the seawater.

A third scenario utilizes a second evaporative crystallizer to treat the bittern and effluent from the Mg recovery process. The effluent from Mg recovery is pre-concentrated in a vapor-compression evaporator and then combined with the bittern for crystallization by vapor compression. Recovery of all of the condensate from vapor compression brings the total yield of freshwater close to 100%. Figure 4 shows the process flow streams for the system with ZLD, and table 3 shows the material balance.

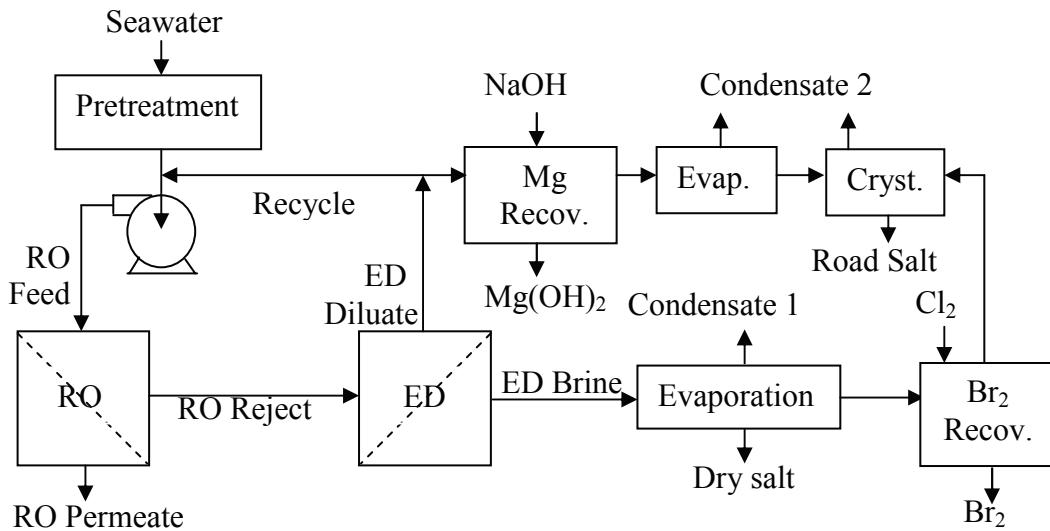


Figure 4. Flow Sheet of Scenario for Zero Liquid Discharge.

Table 3. Material Balance with Partial Seawater Softening, 60% of ED Diluate Recycled to RO Feed, Mg(OH)₂ Precipitation with NaOH, Br₂ Recovery, and Evaporation of Residual Liquids

Stream	Flow L/sec	Ionic Composition (millimolar)							
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Cl ⁻	Br ⁻	SO ₄ ⁼	HCO ₃ ⁻
Seawater	196	459	9.72	52.3	9.98	535	0.87	27.6	2.31
RO Feed	260	375	7.86	80.1	3.1	449	0.65	48.7	0.82
RO Permeate	130	7.13	0.15	0.61	0.023	8.32	0.012	0.090	0.031
RO Reject	130	742	15.57	160	6.1	890	1.30	97	1.62
ED Diluate	107	56	2.19	172	5.7	184	0	113	0.85
Recycle	54	56	2.19	172	5.7	184	0	113	0.85
Mg Recov. Outlet	54	398	2.19	1	5.3	184	0	113	0.40
ED Brine	23	3,950	78.1	102.9	8.2	4,190	7.37	25.9	5.2
Condensate 1	18	0	0.0	0.0	0.0	0	0	0.0	0.0
Bittern	3.8	2,000	466	613	49	3,410	43.9	154.3	31.1
Br Recov. Outlet	3.8	2,000	466	613	49	3,450	2.2	154.3	31.1
Condensate 2	57	0	0	0	0	0	0.00	0	0

4.9 Task 9 – Prepare a Cost Analysis for the Entire Process

The purpose of this task was to assess the economic feasibility of the proposed ZDD process. The capital equipment costs for the analysis were based on reported costs of the individual processes, not a detailed design of the entire plant. Operating costs were based on data from the process model. The WaTER computer program was used to estimate the cost of RO treatment (Wilbert, 1999). Most of the cost estimates in the WaTER program were based on a study by Gumerman, et al. (1979). The version of WaTER used here had cost indices updated to April 1, 2002. Calculations for RO power and for energy recovery were based on data by Gelsler (2001). Costs for brine concentration and salt crystallization were based on a case study by Ericsson (1996). The price of ED stacks was based on a budget estimate provided by a representative of Tokuyama Corp (Matsunga, 2003), and the price of auxiliary components for the ED was estimated to be equal to the stack price. The cost of bromine production was based on a capital expenditure of \$1 million and the consumption of a stoichiometric amount of purchased chlorine. The estimated value for recovered salt and water products were obtained from quoted commodity prices (free on board plant) per metric ton: water: \$0.60 (\$2.27 per kilogallon [kgal]), NaCl: \$60, Mg(OH)₂ as Mg: \$673, and Br₂: \$900.

It should be emphasized that the economic analysis given in this report is very preliminary and that other costs will certainly arise as the processes are developed further. However, the preliminary results are encouraging in that they indicate that the recovered products can be sold for prices that will cover the cost of their recovery. Table 4 shows the economic analysis for the scenario represented by table 1 wherein there is only sand filtration of the seawater as pretreatment for RO.

Table 5 shows the economic analysis for the scenario represented by table 2 wherein the seawater is subjected to partial softening by the addition of Na₂CO₃ to selectively precipitate Ca. The quantity of Mg recovered is lower in the scenario that includes pretreatment, because some of the Mg is precipitated in the pretreatment process. However, the quantity and quality of the NaCl is improved, and a higher selling price of \$60 per metric ton is attributed to this salt versus \$55 per ton for the salt from the scenario that does not include seawater softening.

The economic analysis indicates that the additional value of products recovered does not support the cost of the pretreatment, but partial softening allows discharge of a stream with the same density as seawater, and it would likely improve the reliability of the RO process. The use of ED to recover salt eliminates the need for brine disposal and produces NaCl with a market value that more than offsets its cost of recovery.

Table 4. Economic Analysis with Sand Filtration of Seawater

Unit	Material Recovered	Annualized Capital Cost	Annual Operating Cost	Annual Value of Product
Pretreatment RO Unit		\$11,000 \$377,000	\$18,000 \$1,370,000	
	Potable water			\$2,460,000
Electrodialysis Crystallization		\$1,654,000 \$209,000	\$3,431,000 \$1,737,000	
	NaCl Potable water			\$9,121,000 \$363,000
Bromine Unit	Bromine	\$87,000	\$66,000	\$405,000
Mg(OH) ₂ Unit	Mg(OH) ₂	\$61,000	\$1,973,000	\$6,616,000
Totals		\$2,400,000	\$8,600,000	\$19,000,000
Profit				\$8,000,000

Table 5. Economic Analysis with Partial Seawater Softening

Unit	Material Recovered	Annualized Capital Cost	Annual Operating Cost	Annual Value of Product
Pretreatment RO Unit		\$65,000 \$374,000	\$850,000 \$1,345,000	
	Potable water			\$2,460,000
Electrodialysis Crystallization		\$1,644,000 \$197,000	\$3,401,000 \$1,592,000	
	NaCl Potable water			\$9,158,000 \$331,000
Bromine Unit	Bromine	\$74,000	\$62,000	\$381,000
Mg(OH) ₂ Unit	Mg(OH) ₂	\$52,000	\$1,661,000	\$5,564,000
Totals		\$2,400,000	\$8,900,000	\$17,900,000
Profit				\$6,600,000

The final scenario that was developed included evaporation of all of the water in the discharge streams to make salable condensate and road salt. The material balance for this ZLD system (shown in table 3) indicates 99% water recovery. The cost analysis for the final evaporation (shown in table 6) is based on electrically driven vapor compression with reported electrical energy input of 18.5 kilowatthours per cubic meters of water evaporated (Erickson, 1996). The value of the road salt and condensate recovered support only about half of the costs of the final evaporation, but the overall process still shows a profit.

Table 6. Economic Analysis of ZLD System

Unit	Material Recovered	Annualized Capital Cost	Annual Operating Cost	Annual Value of Product
Pretreatment		\$65,000	\$853,000	
RO Unit		\$375,000	\$1,351,000	
	Potable water			\$2,460,000
Electrodialysis		\$1,640,000	\$3,390,000	
Crystallizer 1		\$199,000	\$1,617,000	
	NaCl			\$9,159,000
	Potable water			\$337,000
Bromine Unit		\$84,000	\$62,000	
	Bromine			\$383,000
Mg(OH) ₂ Unit		\$52,000	\$1,683,000	
	Mg(OH) ₂			\$5,641,000
Evaporator		\$484,000	\$2,701,000	
Crystallizer 2		\$178,000	\$1,616,000	
	Road salt			\$1,445,000
	Potable water			\$1,071,000
Totals		\$3,100,000	\$13,300,000	\$20,500,000
Profit				\$4,100,000

5. Conclusions and Recommendations

The results of this preliminary study indicate that the use of electrodialysis to recover salts from the reject stream of seawater RO can reduce the potential detrimental impact of discharging the reject stream to the ocean. If fully implemented, the process could produce high-purity NaCl, Mg(OH)₂, Br₂, and mixed dry salts with zero liquid discharge. One of the challenges for concentrate disposal to the ocean is that the density of RO concentrate is greater than the density of seawater. Without proper mixing, the denser concentrate forms a plume that falls toward the sea bottom. Some organisms within the plume may be adversely affected by the higher salt levels from the RO concentrate. The concentrate stream can be made more acceptable for return to the ocean by simply removing NaCl with ED treatment to reduce the salinity to a level that has approximately the same density as seawater. This study demonstrated that ED can make that needed reduction in salinity. Furthermore, use of ED with ion-exchange membranes that are selectively permeable to monovalent ions, notably Na⁺, K⁺, Cl⁻, and Br⁻, produces a concentrated salt stream that is especially useful as a source for high quality NaCl salt. In the laboratory study, brine from the ED had a salt concentration of 20% or greater compared to 7% in the RO reject; therefore, substantially less thermal energy was required to evaporate water to crystallize the NaCl salt.

A mathematical model was prepared to describe the material balance, energy balance, and process economics; and results were reported for scenarios based on a 3-mgd RO system. The economic model indicates that NaCl salt is the most lucrative product of the process, and its value offsets the cost of its recovery. Recovering Mg(OH)₂ by precipitation with NaOH and bromine by adding chlorine both appear to be economical, based on the cost of chemicals and capital equipment. The least expensive scenario examined was the removal of enough NaCl by ED to allow the recycle of half of that stream to the RO feed and discharge of the remainder to the ocean. Partial softening of the seawater (discussed below) reduces projected profits somewhat but would likely be necessary to protect the RO membranes. Evaporation of all of the water from the residual liquid streams is not supported by the value of potable water and road salt produced, but the resulting ZLD system would still be profitable.

Excessive osmotic pressure generally limits water recovery from seawater by RO to about 50%, but salt removal from the RO reject can increase water yield. Since the salinity of the ED diluate is the same as or lower than seawater, a portion of the diluate could be returned as RO feed to reduce the amount of seawater that needs to be treated and further increase the yield of freshwater. ED produces brine composed of 20% salts and 80% water of hydration of the electrically transported ions. The water in the brine represents 9% of the water in the RO feed. Most of the water in the ED brine is recovered as condensate from the evaporator, so the overall yield of freshwater from seawater is increased to 58%. The diluate from the ED has more than twice the Mg content of seawater, which

makes it a resource for Mg recovery before return to the ocean. A mathematical model of the ZDD process indicates that recycling half of the diluate to the RO feed reduces the input of seawater enough to raise the yield of potable water to 76%.

Without pretreatment to remove calcium from the incoming seawater, the recycling of a large portion of the ED diluate would lead to precipitation of calcium salts, primarily CaCO_3 and CaSO_4 , within the membrane equipment. This problem can be avoided by pretreatment of the seawater to remove calcium. The mathematical model indicates that partial softening to remove 75% of the calcium would allow recycle of 60% of the ED diluate and increase the yield of potable water to 79%. Experiments on the pretreatment of seawater were not within the scope of this study, but experiments with the NaCl-depleted solutions produced by ED demonstrate that Ca can be removed by adding Na_2CO_3 .

There is a compelling benefit to removing calcium in the pretreatment to RO rather than later in the process. The low levels of calcium in the RO feedwater would eliminate any concerns of CaSO_4 precipitation. Even though the calcium would not be completely removed in the pretreatment, it would remain soluble during the precipitation of $\text{Mg}(\text{OH})_2$ because of its much higher solubility at high pH.

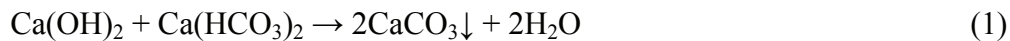
Although calcium and magnesium are lumped together in most discussions about hardness and they are similar in their transport through membranes, their water solubility properties are vastly different as shown in the table below. The sulfate and carbonate salts of magnesium are roughly 100 times more soluble than the calcium salt, but $\text{Ca}(\text{OH})_2$ is about 200 times more soluble than $\text{Mg}(\text{OH})_2$. The solubilities (grams per 100 grams of water) of calcium and magnesium salts are shown in the table below (temperatures in degrees Celsius are shown as superscripts).

	Calcium	Magnesium
Sulfate	0.209 ⁰	26 ⁰
Carbonate	0.0015 ²⁵	0.129 ²⁵
Hydroxide	0.185 ⁰	0.0009 ¹⁸

Data from *CRC Handbook*, 39th edition.

CaSO_4 scale is a problem in many desalination processes, and the ZDD process is no exception. Without prior softening of the seawater, the higher concentrations of Ca^{++} and SO_4^- ions in the recycled ED diluate will make the RO more prone to scale formation. Some method for removing Ca^{++} or SO_4^- would be required to avoid scale formation, preferably as a pretreatment process. It should be noted that scale inhibitors added to the seawater before RO treatment would be retained in the NaCl-depleted stream from the ED at elevated concentrations.

Since Ca^{++} ions are present in a molar concentration less than half that of SO_4^- ions, calcium removal would be more efficient than sulfate removal. Furthermore, the concentration of Ca^{++} ions is only one-fifth that of Mg^{++} ions, and magnesium is to be removed at a later stage in this ZLD process. A process is needed to selectively remove calcium from the seawater without removing appreciable amounts of magnesium. Nanofiltration and conventional lime-soda softening remove calcium and magnesium, so neither process would be appropriate if Mg is to be recovered from the ED diluate. However, selective softening with soda ash (Na_2CO_3) would be appropriate. Calcium concentrations as low as 0.4 millimolar per liter (mmol/L) can be achieved with lime-soda softening [El-Manharawy, 2002], and similar results would be possible with selective soda ash softening. It follows that 96% removal of calcium from seawater containing 10 mmol/L calcium content should be possible. The reaction sequence would be adding a base to convert the seawater bicarbonate ions to carbonate followed by adding sufficient soda ash to achieve the optimum calcium removal without excessive precipitation of magnesium carbonate. The base could be lime or caustic soda.



Caustic soda is more expensive than lime, but it removes twice as much calcium as lime does per unit of alkalinity while producing the same quantity of precipitate. Assuming stoichiometric utilization of the bicarbonate alkalinity in seawater, caustic soda would cause precipitation of 23% of the calcium as compared to 11.5% when using lime. The remainder of the calcium removal would be accomplished with adding soda ash.



Complete removal of calcium as CaCO_3 would require excess soda ash, and that would lead to precipitation of magnesium carbonate. Fortunately MgCO_3 is much more soluble than CaCO_3 , so the reduction in magnesium content should not be excessive.

Although selective softening by adding Na_2CO_3 to remove Ca from seawater is straightforward and likely to succeed, the cost of chemicals is significant. An alternate (and unproven) technology that could be less expensive is using selective ion exchange to remove Ca from seawater. Cation-exchange resins have a stronger affinity for Ca^{++} than for Mg^{++} , so operating a softening bed past the point of Mg^{++} breakthrough and to the point of Ca^{++} breakthrough would load the bed primarily with Ca^{++} . Then, the bed could be regenerated with the bittern from the NaCl crystallizer.

Selective removal of calcium might be achieved with a modified form of the Carix process, which uses a mixed bed of weak-acid and strong-base resins

regenerated with CO_2 . The Carix process was used successfully in Germany to treat hard brackish water (Hoell and Feuerstein, 1985). The modification would be to continue the ion-exchange process past the point of magnesium breakthrough and stop at the point of substantial calcium breakthrough. Weak-acid cation resins are known to have a selectivity sequence of $\text{H} \gg \text{Na} > \text{Ca} > \text{Mg}$. Regeneration with CO_2 (H_2CO_3) converts the weak-acid cation resin to the H form, and contact with slightly alkaline seawater converts it to the Na form. The Na is displaced first with Mg because of its higher concentration, and then the Mg is displaced with Ca because of its higher affinity.

It is recommended that further research be conducted to demonstrate both precipitation and ion-exchange methods for pretreatment of seawater for selective removal of calcium to determine the extent to which water recovery can be increased when pretreatment is employed and to select which of the two pretreatment processes is more economical.

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