Zero Liquid Discharge Desalination of Brackish Water with an Innovative Form of Electrodialysis: Electrodialysis Metathesis

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Water treatment by desalination is increasing worldwide to meet growing water demands, preserve the value of reclaimed water, provide drought proof supplies, and protect public health and aquatic ecosystems from emerging contaminants. Implementing desalination, however, can be constrained by the challenge of managing the concentrate byproduct generated when water is desalinated by membrane processes.

The options for managing concentrate are:
- Direct discharge
- Deep well injection
- Discharge to a wastewater treatment facility
- Zero liquid discharge

Discharge options that fail to remove salts and contaminants from the water cycle increasingly are considered unsustainable. In zero liquid discharge (ZLD) desalination, concentrate is treated to produce product water and there is no discharge of liquid waste from the process.

Currently ZLD desalination is applied primarily to industrial waste streams or power plant cooling water. The established technologies for ZLD are thermal desalination and evaporation ponds. Each has disadvantages that can make its use prohibitively expensive for drinking water applications.

Research was conducted to evaluate ZLD desalination of brackish water using a new electrodialysis technology referred to as electrodialysis metathesis (EDM). The goal of this work was to reduce the costs and energy requirements for ZLD desalination.

The ZLD treatment approach is illustrated in Figure 1. Concentrate from reverse osmosis (RO) is desalinated with EDM to generate a product stream and two EDM concentrate streams. Concentrate from EDM is treated with thermal desalination, in this case a mechanical vapor compression crystallizer.

The water sources evaluated in this project are in Florida, where the wet climate precludes use of evaporation ponds. In arid climates, evaporation ponds could be an economical alternative to thermal desalination as the final ZLD step. The final product water is

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a blend of RO permeate, EDM diluate, and crystallizer distillate.

Electrodialysis has been used for decades to remove ions from water. In drinking water applications, the objective is to produce desalinated water for potable use. In the chemical and food industries, electrodialysis has been used to concentrate solutions to recover valuable salts or brine products and to produce chemical products.

The process is illustrated in Figure 2. A conventional electrodialysis stack comprises alternating cation and anion selective membranes between a cathode and anode. The driving force is the electric potential gradient between the anode and cathode. Anions are drawn toward the positively charged anode, and cations are drawn toward the negatively charged cathode.

Cations pass through the negatively charged cation exchange membrane and are rejected by the positively charged anion exchange membrane. Similarly, anions pass through the anion exchange membrane and are rejected by the cation exchange membrane. As a result, water flowing through alternate compartments is depleted of ions and concentrated with ions.

In terminology typically used in the electrodialysis industry, the solution being depleted of ions is referred to as diluate, and the solution receiving ions is referred to as concentrate. The basic unit of electrodialysis is a cell pair comprising a diluate compartment, a concentrate compartment, an anion exchange membrane, and a cation exchange membrane. A typical electrodialysis stack contains hundreds of cell pairs.

Figure 1 – Zero Liquid Discharge Desalination with Electrodialysis Metathesis (EDM)

Figure 2 – Conventional Electrodialysis Has Repeating Units of Two Compartments and Two Membranes
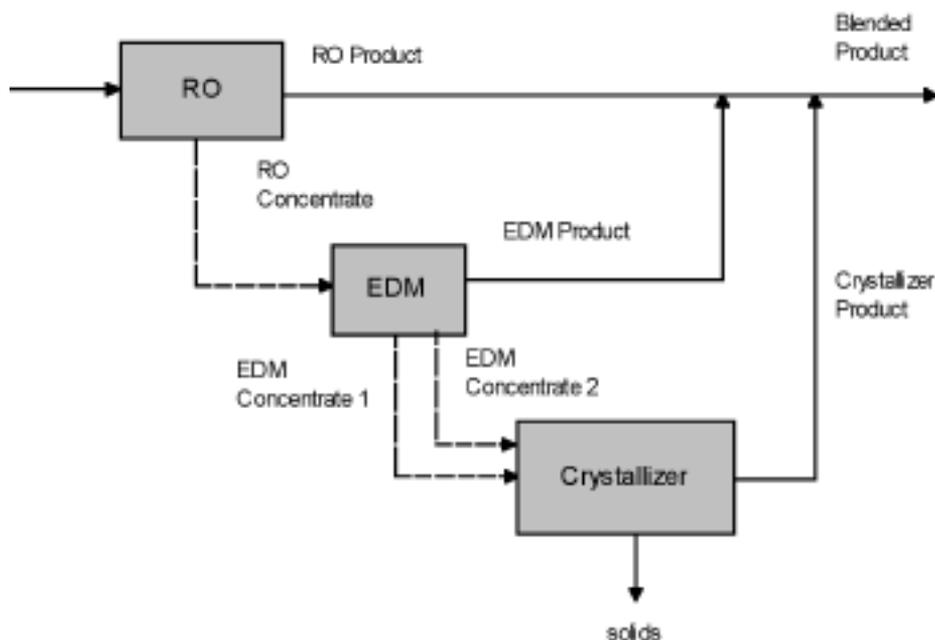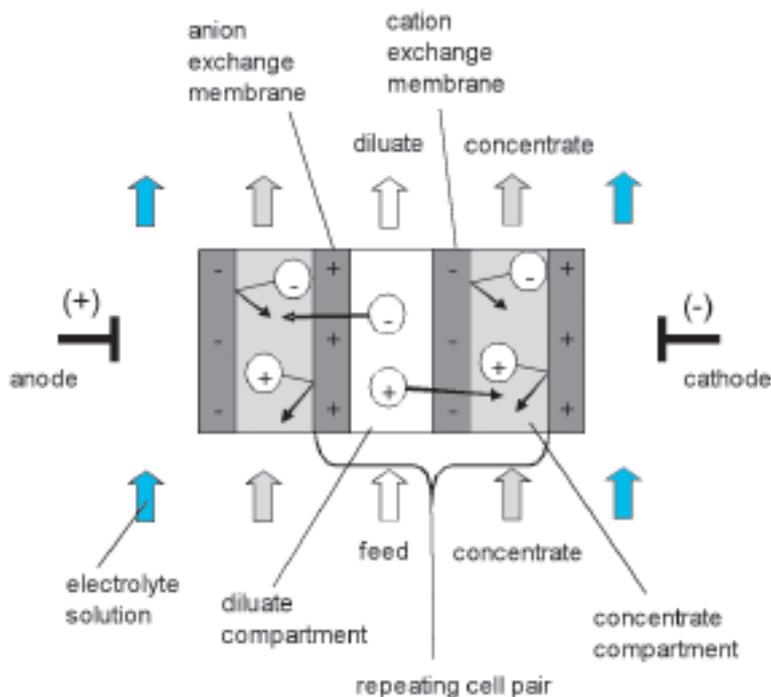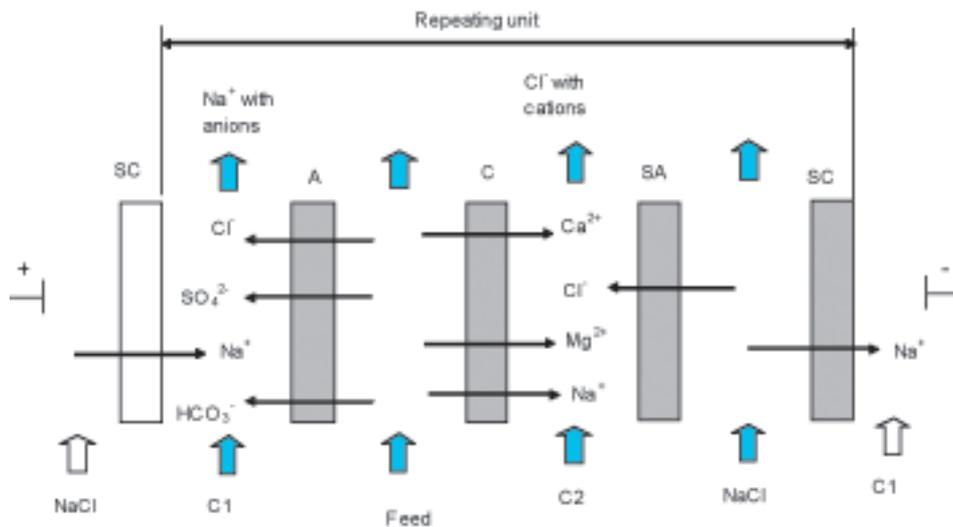

Figure 2 – Conventional Electrodialysis Has Repeating Units of Two Compartments and Two Membranes

Figure 3 – Electrodialysis Metathesis Has Repeating Units of Four Compartments and Four Membranes.

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Table 1 - EDM Stack Description	Component	Description
	Cation exchange membranes	5 CMX
		5 CMS
	Anion exchange membranes	5 AMX
		5 ACS
	Active membrane area per cell	0.02 m^2
	Total active cell area	0.1 m^2
	Anode	Ti/Pt
	Cathode	Stainless steel

Electrodialysis has been tailored for specific goals through the arrangement of membranes and the use of specialty membranes. Bipolar membranes have been used to produce acid and base, HCl and NaOH, from NaCl (Mazrou et al., 1998; Wilhelm et al., 2002). Japan, Korea, and Taiwan use electrodialysis followed by evaporative crystallization to produce table salt from seawater (The Salt Industry Center of Japan 2009). Alheritiere, Ernst, and Davis (1998) proposed using it to produce magnesium sulfate and sodium chloride from magnesium chloride and sodium sulfate.

EDM was evaluated for treatment of RO concentrate in this research. The primary difference between EDM and electrodialysis is the use of four solution compartments and four membranes, rather than two of each in the repeating unit.

The EDM membrane configuration is shown in Figure 3. The repeating unit comprises one diluate compartment, two concentrate compartments, one NaCl solution compartment, one ordinary anion exchange (A), one ordinary cation exchange (C), one monovalent selective anion exchange (SA), and one monovalent selective cation (SA). This unique configuration is designed to separate EDM concentrate into two streams of highly soluble salts: one containing sodium with anions and the other containing chloride with cations.

This characteristic of EDM provides a significant advantage in treating RO concentrate because the membrane-fouling potentials of typical scalants such as $CaSO_4$ and $CaCO_3$ do not increase with recovery, as is the case with RO, nanofiltration, and other forms of electrodialysis, such as electrodialysis reversal (EDR).

Methods

In this experiment, a pilot skid was used to evaluate EDM treatment of nanofiltration, RO, and EDR concentrate samples from four desalination water treatment plants. Two of the concentrate samples had high total organic carbon concentrations (> 50 mg/L), and these samples were pretreated with ion exchange (MIEX®) for total organic carbon reduction.

The EDM pilot stack components are described in Table 1. The active area of each membrane was 10 centimeters wide and 20 centimeters long. The stack contained five repeating units, and the total active EDM membrane area for the stack was 0.1 square meter. The ion selective membranes were NEOSEPTA® by the Tokuyama Corporation.

The EDM unit contained rotameters for

Table 2 – Average Raw Water Quality of the Sources Evaluated

Analyte	Units	TGW	LHGW	CGW	OGW	AR	SJR	IR
Ca	mg/L	120	210	231	120	40	53	319
Mg	mg/L	21	200	114	15	12	22	1100
Na	mg/L	70	1400	54	65	30	158	8360
K	mg/L	6	67	4	3		7	324
Fe	mg/L	0.02	0.02	0	0.22		0.14	0.49
Mn	mg/L	0.003	0.003	0	0.01	0.01		0.01
Ba	mg/L	0.02	0.03	0.017	0.02	0.03	0.03	0.04
Sr	mg/L	0.68	16	13	0.5		1.5	7.6
Al	mg/L	0.05	0.05	0.17		0.28		0.54
Cl	mg/L	100	2800	97	130	27	285	13,600
SO_4	mg/L	50	730	722	250	80	90	2100
HCO_3	mg/L	378	207	166	329	109	55	148
NO_3	mg/L	>2.5	0.5	0	0.01	5		8.4
F	mg/L	0.4	2.2	1.4	0.19	10		0.15
SiO_2	mg/L	3.4	16	25	20	10	5	1.3
TDS	mg/L	560	5300	1412	630	270	750	28,700
TOC	mg/L	8.0	2.0	2.7	7.2	11	20	10.7
Ph	SU	7.4	7.4	7.3	7.4	7.6	7.5	7.7

Table 3 – EDM Pilot Water Quality Results with Lower Hawthorn Aquifer RO Concentrate

Analyte	RO Concentrate (mg/L)	EDM Feed (mg/L)	EDM Concentrate 1 (mg/L)	EDM Concentrate 2 (mg/L)
Calcium	450	322	34	10,200
Magnesium	500	417	9	6500
Sodium	4700	4200	60,800	37,900
Chloride	7800	6280	65,800	102,000
Sulfate	2580	2220	34,200	nondetect
Silica	43.5	49.0	16	11

Table 4 – Power Consumption in the EDM Pilot Tests

Source	Current (A)	Voltage applied to stack (V)	Voltage drop at electrodes (V)	Voltage per cell (V)	Power (W/cell)
TGW	1.9	8	4.22	0.76	1.4
LHGW	3.0	8	4.80	0.60	1.8
CGW	1.4	8	3.96	0.81	1.1
OBGW	1.7	8	4.01	0.80	1.4

flow measurement and pressure sensors on the feed, concentrate, and electrolyte streams. All flows and pressures were recorded regularly. Voltage and current were displayed continuously on the EDM control panel, and these measurements were recorded regularly.

The stack was operated at 8 volts (0.6 to 0.8 volts per cell after accounting for voltage drops at the electrodes). Conductivity was measured regularly in the feed, electrolyte, and concentrate tanks using a handheld conductivity meter. Samples were collected periodically for laboratory analysis of the feed, concentrate, and electrolyte streams.

Raw-water quality characteristics of the sources evaluated are shown in Table 2. EDM pilot testing was conducted with concentrate generated from desalination of the first four sources in the table. The pilot results were used to conduct desktop evaluations of the remaining three sources.

Results & Discussion

EDM was pilot tested with concentrate samples from existing desalination plants. The total dissolved solids range of the concentrate samples was 3,000 to 16,000 milligrams per liter, and the samples were supersaturated with salts that would foul RO or electrodialysis membrane systems if either were used for further treatment.

Water quality and EDM performance parameters were monitored to evaluate: 1) the effectiveness of EDM in separating the concentrate into two streams of highly soluble salts, 2) the rate of product water recovery by EDM, and 3) energy requirements for desalination with EDM.

Water quality results for EDM pilot tests with one of the water sources are shown in Table 3. Electrodialysis with EDM separated concentrate into two streams of highly soluble salts. Concentrate Stream 1 contained high concentrations of sodium, chloride, and sulfate with low concentrations of calcium and magnesium. Concentrate Stream 2 contained high concentrations of chloride, calcium, magnesium, and sodium. Effective separation of the concentrate into two highly soluble streams was observed in all tests with all water sources.

Recovery of product water during EDM pilot tests ranged between 99.8 and 99.9 percent. Recovery in electrodialysis is governed by the rate of water transfer by osmosis and electroosmosis from the diluate and electrolyte solution cells to the concentrate cells. The transfer rate in these experiments ranged between 7.4 and 8.2 moles of water per equivalent transferred and is consistent with reported

values for other forms of electrodialysis.

Power consumption during the EDM pilot tests is shown in Table 4. Current in electrodialysis is proportional to the number and charge of ions removed from the diluate. Current is related to voltage and resistance by Ohm's Law, and power is the product of current and voltage.

Test results were used to estimate full-scale ZLD treatment costs for seven water sources using the EDM method, and these costs were compared to the established ZLD method using thermal desalination illustrated in Figure 4. The treatment criterion for each system was a blended water total dissolved solids of 400 milligrams per liter or less.

The two factors that determined the economics of this ZLD approach were EDM recovery and EDM energy consumption. Each of these factors depended primarily on feed water total dissolved solids.

Figure 5 shows the effect of total dissolved solids on EDM recovery. The water lost as concentrate during desalination with EDM is proportional to the quantity of ions removed. Consequently, EDM recovery decreased as feed water total dissolved solids and the EDM desalination requirement increased.

Figure 6 shows the effect of raw water total dissolved solids on the EDM energy consumption. The energy required for desalination with electrodialysis is proportional to the quantity of ions removed; consequently, EDM energy increased in proportion to total dissolved solids. Typical energy required for treatment of RO concentrate with a brine concentrator is 20 kilowatt hour per cubic meter.

Figure 7 shows treatment costs for ZLD with EDM compared with treatment costs for the currently established ZLD method using thermal desalination. The treatment costs are per cubic meter of RO concentrate recovered, and the costs comprise annual operations and maintenance costs and capital costs amortized over 20 years at 6 percent interest. Energy costs were estimated using an electricity cost of $0.12 per kilowatt hour.

The energy required for electrodialysis depends on ionic concentration while the energy required for thermal desalination predominantly depends on the volume of water evaporated; consequently, treatment costs increased more rapidly with TDS for EDM than for thermal desalination. For raw water total dissolved solids of 3,000 milligram per liter or less, the EDM method was significantly less expensive than ZLD with thermal processes. The costs appear to be comparable in the 5,000 to 10,000 milligrams per liter total dissolved solids range and to favor thermal desalination above 10,000 milligrams per liter total dissolved solids.

This research indicated that the use of electrodialysis with EDM is very promising for zero liquid discharge desalination of brackish water sources containing 5,000 milligrams per liter total dissolved solids or less. Above 10,000 milligrams per liter concentrations, energy requirements begin to shift the economics in favor of thermal desalination. Specific findings were:

♦ Prior to testing, the effectiveness of EDM in separating concentrate into two streams of highly soluble salts was recognized as a key

Figure 4 – ZLD Desalination with Thermal Devices

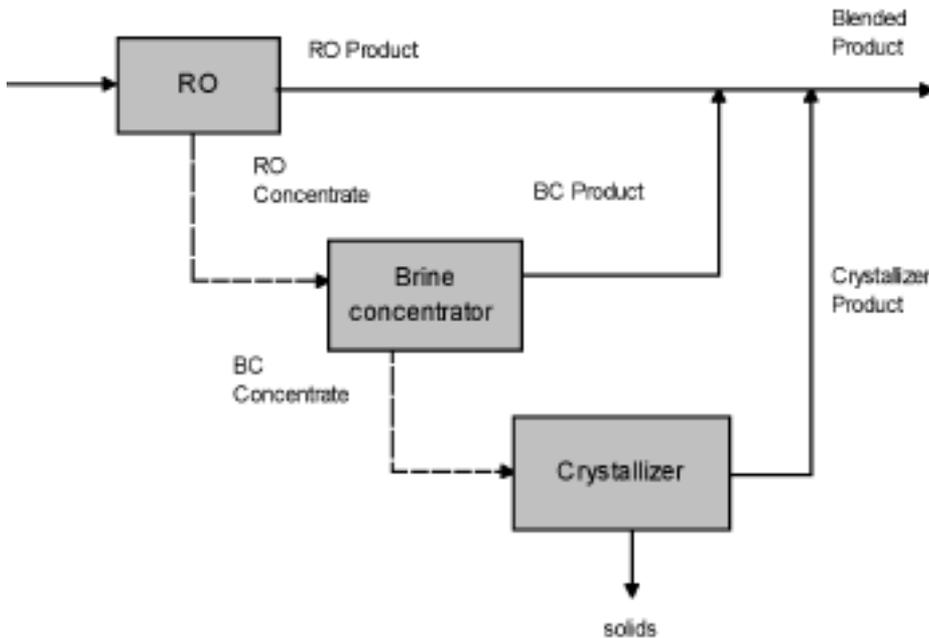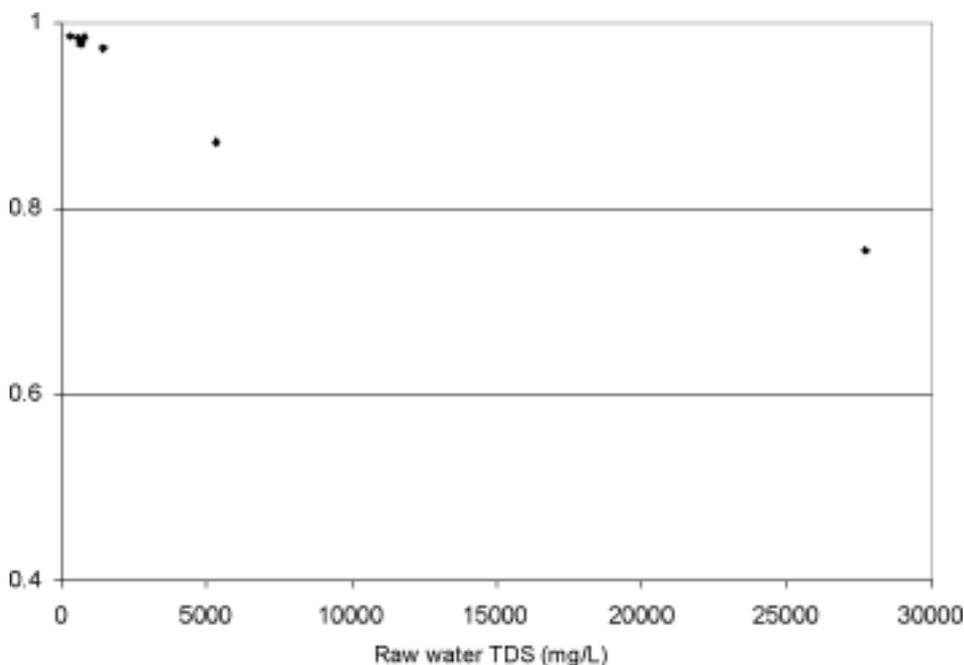## Figure 5 – Effect of Raw Water TDS on EDM Recovery

to its success treating RO concentrate. The pilot tests demonstrated that EDM was highly effective in separating concentrate into two streams: one containing sodium and anions and the other containing chloride and cations.

- ♦ Recovery of product water by the EDM pilot treating RO, nanofiltration, and EDR concentrate samples ranged from 99.8 to 99.9 percent.
- ♦ Power consumption by the EDM pilot ranged from 1.1 to 1.8 watts per EDM cell.
- ♦ No inorganic or organic compound concentrations were found in any of the EDM streams that would be considered potential membrane fouling threats. There was no variation in the EDM pilot pressures or flows in any of the experiments. It was concluded that the EDM pilot treated primary RO concentrate from the sources without fouling the EDM membranes.
- ♦ ZLD treatment costs for EDM followed by a crystallizer ranged from $0.64 to $11.21 per cubic meter of concentrate recovered and were dependent on total dissolved solids concentration of the water. Treatment costs ranged from $0.64 to $0.90 per cubic meter treated for water sources with total dissolved solids less than 1,500 milligrams per liter, $4.20 per cubic meter treated for water sources with 5,300 milligrams per liter, and $11.21 per cubic meter for water sources with 28,000 milligrams per liter. By comparison, treatment costs using conventional ZLD were approximately $3 per cubic meter treated for water sources with total dissolved solids less than 1,500 milligrams per liter, $4 per cubic meter for water sources with 5,300 milligrams per liter, and $7 per cubic meter for water sources with 28,000 milligrams per liter.

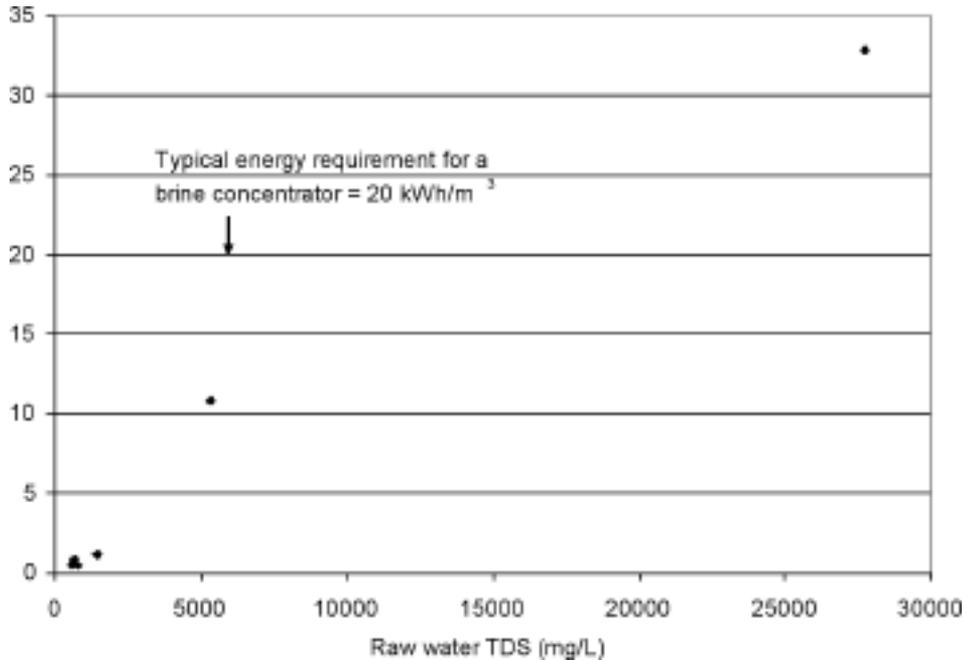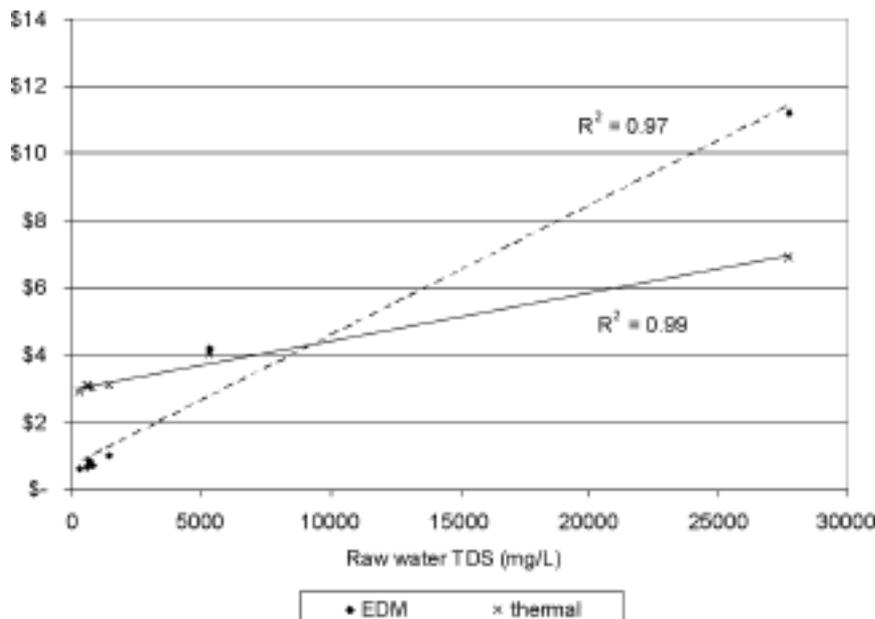Figure 6 – Effect of Raw Water TDS on Energy Required for EDM

Figure 7 – Effect of Raw Water TDS on Relative Costs for EDM and Thermal Conclusions

Acknowledgments

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