Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1041162

57 (2016) 11029–11039
May

Taylor & Francis
Taylor & Francis Group

High-recovery electrodialysis reversal for the desalination of inland brackish waters

Connor Hanrahan[a], Leila Karimi[b,*], Abbas Ghassemi[b], Ali Sharbat[c]

[a]*General Electric Water and Process Technologies, Charleston, SC, USA, email: connorphanrahan@gmail.com*
[b]*Institute for Energy & the Environment (IEE), New Mexico State University, Las Cruces, NM, USA, Tel. +1 575 646 3075; emails: lkarimi@nmsu.edu (L. Karimi), aghassem@nmsu.edu (A. Ghassemi)*
[c]*Civil Engineering Department, California State Polytechnic University, Pomona, CA, USA, email: sharbat@csupomona.edu*

Received 9 November 2014; Accepted 11 April 2015

ABSTRACT

Since the inland disposal of large volumes of desalination concentrate is environmentally and financially impractical, a high-recovery desalination design is required to reduce concentrate volume. In practical applications, recovery is limited by scale formation from minimally soluble salts, which acids and antiscalant compounds can inhibit only temporarily. Therefore, the risk of scale formation, which is governed by the system's electrochemical behavior, determines the high-recovery potential of desalination technologies. In this research, high recovery was investigated using a pilot-scale electrodialysis reversal (EDR) system and natural feedwaters from a deep aquifer at the Brackish Groundwater National Desalination Research Facility in Alamogordo, NM. Experiments were performed to identify the maximum permissible $CaSO_4$ saturation levels during long-term, continuous operation with antiscalant dosing. The results indicated that EDR has enormous potential for treating $CaSO_4$-rich inland brackish waters and that EDR may not be severely limited by the risk of scale formation in the hydrodynamic/concentration boundary layer. Long-term operation saturation indices were achieved, which were significantly greater than previously published values, and the system's eventual failure point provides insight into the hypothesized operating conditions. Therefore, the obtained results for high-recovery inland brackish water EDR determined the highest permissible $CaSO_4$ saturation index during long-term, continuous system operation.

Keywords: Electrodialysis reversal; High recovery; Calcium sulfate; Saturation index; Antiscalant

1. Introduction

Fueled by rapid population growth, much of the southwestern United States is experiencing an increased demand on its limited freshwater supply. Consequently, the region is looking toward its extensive brackish water resources to address this issue. In Texas, there are approximately 2.7 billion acre-feet of brackish groundwater [1,2], and in New Mexico, it is estimated that 75% of the groundwater is too saline for most uses without desalination [3]. With both states experiencing severe drought and water shortages, these large volumes of once-ignored saline water could provide the much-needed relief to

---

*Corresponding author.

existing freshwater supplies [4]. Although inland brackish water desalination has the potential to create "new" water resources in these arid regions, implementation is hindered by the relatively high cost of treating brackish waters—specifically, the costs associated with concentrate management [5].

Since the inland disposal of large volumes of concentrate is both environmentally and financially impractical, a high-recovery desalination system is required to reduce the volume of concentrate [6–8]. In practical applications, the recovery is limited by the potential for scale formation, which occurs as minimally soluble salts accumulate in the concentrate stream [1,9–13] and foul system components as they precipitate and cause scaling. Precipitation can be inhibited by the addition of acid or antiscalant compounds, but not indefinitely [14]. Phosphonate antiscalants are widely used in water treatment formulations as scale and corrosion inhibitors and have been used to effectively inhibit gypsum precipitation in many water treatment systems [15].

The ultimate recovery potential of a desalination technology is determined by the system's electrochemical behavior, which can either reduce or augment the risk of precipitation and scale formation. Of particular importance is the effect of the system's boundary layers, in the regions adjacent to the membrane surfaces. The combined presence of the hydrodynamic boundary layer, caused by viscous forces, and the concentration boundary layer, caused by mass transfer rates through the membranes, create a situation where the most saline volume of water is moving at a very low velocity. This hydrodynamic/concentration boundary layer is where the precipitation risk is greatest, effectively limiting the recovery potential of desalination technologies. For this reason, electrodialysis reversal (EDR) systems employ a periodic polarity reversal feature and turbulence-promoting spacers: periodic polarity reverse effectively zeroes the elapsed residence time, and the turbulence-promoting spacers disrupt the hydrodynamic boundary layer and promote mixing.

In previous studies, EDR has achieved high recoveries during brackish water desalination [14,16] and has been used to increase the recovery of reverse osmosis (RO) concentrate [1,14,17]. EDR shows promise as a viable treatment process for brackish groundwaters and brackish water reverse osmosis (BWRO) concentrate for two primary reasons: (1) The periodic polarity reversal allows the system to operate at higher recoveries, and (2) EDR is more robust than RO with respect to scale-prone salts, turbidity, silica, and biological growth [14,18]. Due to these features, EDR has proven capable of achieving higher recoveries than other existing desalination technologies, but the system characteristics have not been fully quantified. For this reason, this research seeks to identify the high-recovery potential of a commercial-scale EDR system. Given that previous studies were performed with either laboratory-scale equipment [1,14] or non-optimal antiscalants [16,17,19,20], shown in Table 1, it is predicted that the use of pilot-scale components and a $CaSO_4$-specific antiscalant will result in recoveries higher than those previously reported.

For brackish water desalination, high-recovery methods must address the relative prevalence and low solubility of calcium sulfate dihydrate ($CaSO_4{\cdot}2H_20$) and calcium carbonate ($CaCO_3$), which restrict the recovery potential for many inland feedwaters [11,25,26], as seen in Table 2.

Given that $CaCO_3$ precipitation can be controlled by pH adjustment and/or antiscalant addition, $CaSO_4{\cdot}2H_20$ (gypsum) scaling is considered the more important concern for high-recovery operation.

As mentioned before, due to the limitations that minimally soluble salts impose on the recovery of desalination processes such as EDR, and given the high cost of brine disposal in inland desalination plants, investigating the possible limits of the recovery rate and pushing those limits can significantly reduce the total cost of water produced by inland desalination plants. As a caveat, it is worth mentioning that, despite EDR's high recovery rates, the EDR process is limited not only by scaling problems, but also by high energy consumption, especially for brackish waters with high salinities. In a separate study, the researchers compared the specific energy consumption of pilot-scale EDR and RO processes, and their results confirmed that the energy consumption of EDR is significantly affected by the level of salinity at different operating conditions [27].

In this study, high-recovery desalination was researched using a pilot-scale EDR system, natural feedwater, and the maximum tolerable $CaSO_4$ saturation levels in continuous and long-term experiments with antiscalant dosing.

To achieve high recovery rates in EDR systems, it is necessary to recycle the concentrate stream, combining it with makeup water and feeding it into the stack as the inlet concentrate. Although the concentrate recycle ratio can be increased to high values, recovery is limited by a potential scaling problem that arises from the presence of less soluble salts in the concentrate stream: During EDR operation, ions removed from the dilute stream build up in the concentrate stream, and ion concentration increases still further with the input from the concentrate recycle stream.

Table 1
Published maximum saturation index (SI) values for $CaSO_4$

		Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	Cl^{-} (mg/L)	SO_4^{2-} (mg/L)	HCO_3^{-} (mg/L)	SI ($CaSO_4$)	Antiscalant (concentration)	Run (h)
1	RO	680	275	630	1,200	2,410	–	0.99	Flocon 180 (3 ppm)	24
2	RO	760	280	1,152	1,100	2,800	1,342	1.09	Flocon 260 (3 ppm)	24
3	RO	983	604	5,915	2,255	13,532	180	2.99	Flocon 100 (3 ppm)	24
4	EDR	1,440	505	3,000	–	6,130	2,700	2.63	Pretreat Plus Y2 K (10 ppm)	1,600
5	EDR	2,500	729	–	3,150	8,130	1,525	4.71	None	1.5
6	EDR	3,644	1,022	2,500	5,855	8,600	2,064	6.08	SHMP (11 ppm)	300

Note: (1) [21], (2) [22], (3) [23], (4) [24], (5) [19], (6) [16].

Table 2
Published data on various $CaSO_4$-rich waters for further treatment

	Source	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	Cl^{-} (mg/L)	SO_4^{2-} (mg/L)	HCO_3^{-} (mg/L)	SiO_2 (mg/L)	SI ($CaSO_4$)
1	RO concentrate	1,165	530	3,273	5,736	2,659	224	105	1.22
2	RO concentrate	519	238	2,170	2,886	2,164	414	N/A	0.65
3	RO concentrate	959	379	2,024	4,817	2,560	–	87	1.12
4	RO concentrate	1,032	318	991	2,823	1,553	576	N/A	0.85
5	Groundwater	576	296	755	954	2,290	210	77	0.83
6	Agricultural drainage water	461	284	2,780	1,085	6,359	262	N/A	0.87
7	Agricultural drainage water	350	236	1,250	342	3,700	91.6	23.5	0.76
8	Agricultural drainage water	625	198	2,820	3,020	4,520	51.2	37.9	1.24
9	Agricultural drainage water	422	962	9,270	1,910	21,400	146.8	43.2	1.57
10	Seawater	555	1,475	12,000	22,000	2,535	131	–	0.43
11	Well 2, BGNDRF brackish water	544	357	835	550	3,229	297	22	0.96

Note: (1) [17], (2) [28], (3) [20], (4) [29], (5) [5], (6) [26], (7–9) [23], (10) [30].

Therefore, the ions can easily reach the supersaturation state, causing scaling from some salts, such as $CaSO_4$. In high-recovery EDR operation, $CaSO_4$ scaling is considered a serious problem. Consequently, to improve the recovery of EDR systems, it is highly important to conduct pilot-scale experiments that identify the highest possible $CaSO_4$ supersaturation index and antiscalant dosage for long-term EDR operation.

In practical applications, there is no theoretical method for quantifying the optimal antiscalant dose [31]. The complex process of heterogeneous nucleation of brackish waters and the specific hydrodynamic/electrochemical behavior of the system must be better understood before fundamental relationships can be developed. Manufacturers do supply a recommended dose, based on experience and laboratory testing, but this dose may or may not be optimal for a specific application in the field. To precisely determine appropriate dosing, more extensive experimentation is necessary.

2. Materials and methods

2.1. Experimental setup

High-recovery research was performed using a pilot-scale EDR system and natural feedwater from a deep aquifer at the Brackish Groundwater National Desalination Research Facility (BGNDRF), in Alamogordo, NM. Experiments were performed to identify the maximum permissible saturation levels for $CaSO_4$

during the long-term, continuous operation of an EDR system with antiscalant dosing. This objective was accomplished with a research methodology that utilized laboratory experimentation and off-site water analysis to systematically and quantitatively analyze the high-recovery potential of EDR for $CaSO_4$-rich groundwater. The experiments were performed using GE Water and Process Technology's MK-IV-2 EDR Stack, detailed in Table 3.

The utilized pilot-scale EDR unit, which is shown schematically in Fig. 1, works as detailed below. First, the influent source water is split into three streams: feed in, concentrate makeup, and electrode in (electrode rinse solution). The predominate portion of the source water enters the dilute flow-paths as the feed in stream. This water is progressively demineralized until it exits the stack as product water. A smaller portion of the source water becomes the concentrate makeup stream, which combines with the concentrate recycle at the suction end of the concentrate pump and enters the concentrate flow-paths as the concentrate in stream. This stream is progressively concentrated until exiting the stack, where a portion goes to waste as concentrate blow-down and the remainder enters the concentrate recycle. The last part of the source water becomes the electrode in stream. This stream is used to flush the electrode chambers of gases and precipitates, which are formed as part of the electrochemical reactions at the surface of the electrodes. In full-scale EDR, the electrode streams are recycled after passing through the degasifier. Although the electrode rinse solution was not recycled in the utilized pilot-scale system, it was not considered in the recovery calculations. Therefore, the inlet stream was assumed to be the summation of product and concentrate blow-down based on the mass balance equation of the system.

During the high-recovery experiments, GE's Hypersperse MDC-706 antiscalant was dosed to the concentrate stream of the EDR system to prevent the precipitation of low-solubility salts. This antiscalant is a proprietary blend that is meant to target $CaSO_4$ scaling. Among the numerous available antiscalants, the reason for using this antiscalant was the manufacturer's recommendation that it be used for waters with very high levels of $CaSO_4$.

2.2. Experimental design

The experiments were performed to identify the maximum permissible $CaSO_4$ saturation levels during the long-term, continuous operation of an EDR system, since the precipitation of $CaSO_4$ limits high recovery in the desalination of numerous inland brackish feedwaters. A total of 3 high-recovery experiments were performed at varying SI($CaSO_4$) levels (8–10) and at varying antiscalant doses (48–64 ppm dosed to concentrate). The experiments were conducted using brackish groundwater from BGNDRF's sulfate-rich Well 2, whose characteristics are shown in row 11 of Table 2. The feedwater was desalted in each experiment to produce approximately 28.4 L/min of product water and 1.9–2.3 L/min of concentrate blow-down. Each experiment utilized the same stack

Table 3
EDR stack specifications

Type		GE MkIV 2
EDR stack		
	Electrical stages	2
	Cell pairs	40 cell pairs/stage
Ion-exchange membranes		
	Heavy cation-exchange	GE CR67-HMR
	Cation-exchange	GE CR67-LLMR
	Anion-exchange	GE AR204-SZRA
	Membrane dimensions	114 × 60 × 0.6 (cm)
	Spacer model	Mk-IV
	Effective membrane area	0.3 m^2/membrane
Operating conditions		
	Product flow	21.2–28.4 L/min
	Concentrate blow-down flow	1.9–2.6 L/min
	Electrode flow	11.4 L/min
	Voltage	240 V/stage
	Current	45 A/stage

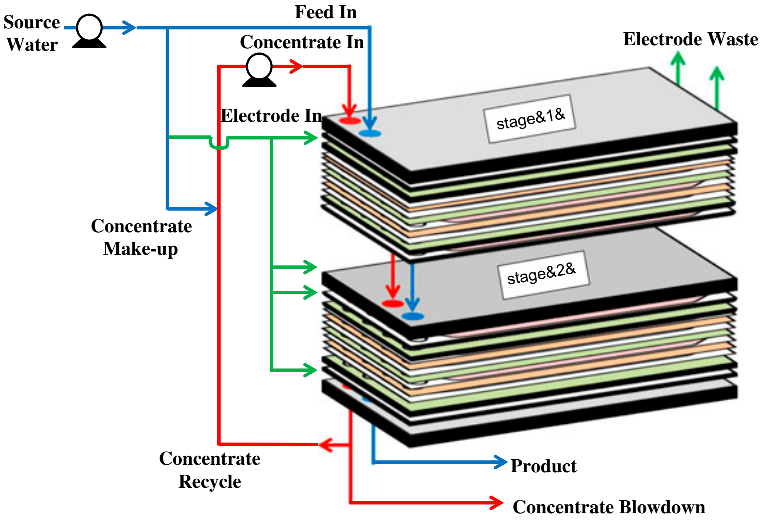

Fig. 1. Schematic of EDR system.

construction, but different operating conditions to achieve the desired SI($CaSO_4$) levels. The experiments were set to run for at least 100 h each, though hydraulic scaling and equipment malfunctions led to a few shutdowns. Between experiments, the system hydraulics were thoroughly washed by a low-pH clean-in-place operation, and the membranes were bathed and scrubbed in low-pH water.

The experiments were designed to outperform the SI($CaSO_4$) limits previously established for EDR and RO operation as shown in Table 1. After determining the desired SI($CaSO_4$) value for each experiment, the optimal antiscalant dose of the EDR concentrate in stream was determined using GE Betz's antiscalant dosing software, "ARGO Analyzer 2.2." This software is designed specifically for RO and determines dosing concentrations for the RO feed. The relationship between the predicted dose to the RO feed and the equivalent dose to the EDR concentrate in stream was determined according the simple relationship between recovery and feed concentration in RO systems as shown in Eq. (1), which assumes 100% rejection of antiscalant.

$$C_C = C_F\left(\frac{1}{1-R}\right) \tag{1}$$

where C_C is the appropriate antiscalant dose to the EDR concentrate in stream (mg/L), C_F is the predicted antiscalant dose to the RO feed stream given by ARGO Analyzer (mg/L), and R is the system recovery determined by the ratio of the product flow rate to the feed flow rate. Although the software was designed for RO systems, it gave a best estimate for the dosing concentrations. The recommended concentration increased with increasing SI($CaSO_4$) levels. The dosing rate of the antiscalant was calculated based on the polarity reversal period. Therefore, the antiscalant dosing was adjusted to attain the desired level of antiscalant at the end of the polarity reversal period when the SI($CaSO_4$) reached the proposed level.

For the chosen SI($CaSO_4$) values, GE EDR predictive software, WATSYS, was used to estimate the required conductivity, calcium ion concentration, and the sulfate ion concentration of the concentrate stream. With this information, a process of data collection and on-site analysis was begun to tune in the appropriate set-points for the EDR system. The optimal experimental voltage setting, polarity reversal period, and concentrate blow-down flow rate were all determined by an iterative method of trial and error to arrive, at the end of the polarity reversal period, at a conductivity which was well-correlated with the desired SI ($CaSO_4$) value. To ensure stable operation at the desired SI($CaSO_4$) value, on-site analyses of calcium hardness and sulfate concentration were routinely performed through the use of HACH analytical tests on samples collected at the end of the polarity reversal period.

2.3. Analytical methods

EDR system conditions were continuously monitored to ensure stable operation. The monitored conditions were the following: hydraulic flow rates, stack voltage and current, pH, temperature, the electrical conductivity of each process stream, and the specific ion composition of selected experimental samples.

Water samples were also collected throughout the long-term experiments to be analyzed for dissolved species. On-site tests of calcium hardness and sulfate concentrations were routinely performed during the experiments to determine the appropriate set-points and to ensure that the system operation was consistent. Dissolved calcium measurements were obtained through a standard EDTA titration, using HACH analytical procedures. Dissolved sulfate was measured through spectrophotometry, according to the HACH SulfaVer 4 Method. For broad species analysis, other samples were periodically collected and analyzed for sodium, potassium, magnesium, calcium, strontium, barium, fluoride, chloride, bicarbonate, nitrate, sulfate, silica, and total organic carbon. During each experiment, water samples were always collected within the final minute of the polarity reversal period, in order to allow enough time for the performance characteristics to stabilize. Before the samples were shipped to the Woodlands facility for composition analysis, they were diluted 10× with deionized water to prevent salt precipitation during transportation.

The saturation index of calcium sulfate was calculated through Eq. (2):

$$\mathrm{SI}(\mathrm{CaSO_4}) = \frac{\gamma_{\pm}{}^{2}\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{SO}_4^{2-}\right]}{K_{\mathrm{sp}}} \tag{2}$$

where $\gamma_{\pm}$, $\left[\mathrm{Ca}^{2+}\right], \left[\mathrm{SO}_4^{2-}\right]$, and K_{sp} are the mean ionic conductivity, concentration of calcium, concentration of sulfate, and thermodynamic solubility product, respectively. The mean ionic conductivity coefficient for the electrolyte was calculated using Eq. (3) as follows:

$$\ln \gamma_{\pm} = v^{-1}(v_X \ln \gamma_X + v_Y \ln \gamma_Y) \tag{3}$$

where $v = (v_X + v_Y)$ denotes the total number of molecules or ions given by one mole of electrolyte and γ_X and γ_Y are cation and anion activity coefficients, respectively. For estimating activity coefficients, the Pitzer model [32] was applied in this research due to its broad applicability and its ability to predict SI levels for salinities up to 6 M [33], which covers the range of the examined experimental conditions (<1.0 M).

3. Results and discussion

Three separate long-term experiments were performed to identify the maximum permissible SI (CaSO4) level for continuous EDR operation. The experimental conditions for each experiment are listed in Table 4; the SI(CaSO4) value was increased sequentially with each experiment. An analysis of the system's operating conditions and the chemistry of the water samples is presented for each experiment.

3.1. Experimental results

3.1.1. Experiment #1

The first experiment was performed to establish a baseline for further high-recovery testing. The experiment was set to operate at $\mathrm{SI(CaSO_4)} = 8$. This value is higher than any published experiment and well outside the manufacturer's recommendations. The experimental operating conditions were determined by iteratively adjusting the voltage, flow rate, and polarity reversal period to reach the desired $\mathrm{SI(CaSO_4)}$ value at the end of the polarity reversal period. The antiscalant dose of 48 ppm, which was added to the concentrate stream, was determined using GE's antiscalant dosing software, ARGO Analyzer, although the program indicated that this $\mathrm{SI(CaSO_4)}$ value was too great for safe operation. The experiment was continuously operated at the conditions detailed in Table 4 in the column for Experiment #1.

The system conditions were monitored throughout the experiment, and data points were collected daily. The system conditions showed no signs of performance decline throughout the experiment.

The chemical compositions of the feed, product, and concentrate streams for the first experiment are given in Table 5. The water analyses showed that an average $\mathrm{SI(CaSO_4)}$ value of 8.16 was achieved at the end of polarity reversal periods in the concentrate stream during 330 h of continuous operation with 48 ppm antiscalant dosing.

3.1.2. Experiment #2

Experiment #2 was set up to target an $\mathrm{SI(CaSO_4)}$ value of 9 ppm at the end of the polarity reversal period. This experiment was continuously operated for 138 h at the conditions detailed in Table 4 in the column for Experiment #2. The system showed no signs of performance decline throughout the experimental run.

The chemical compositions of the feed, product, and concentrate streams for Experiment #2 are given in Table 6. The water analyses show that an average $\mathrm{SI(CaSO_4)}$ value of 8.79 was achieved at the end of polarity reversal periods in the concentrate stream

Table 4
Average daily operating conditions for all experiments

	Experiment	1	2	3
Conductivity (μS/cm)	Feed	6,508	6,313	6,613
	Product	4,553	4,521	4,355
	Concentrate	21,110	20,580	25,000
Electrical (V, A)	Stage 1 voltage (V)	34.4	24.2	29.4
	Stage 1 current (A)	36.1	21.5	31.6
	Stage 2 voltage (V)	<3	17.9	15.6
	Stage 2 current (A)	0	15.6	13.4
Flow rate (L/min)	Product	28.5	28.4	28.8
	Blow-down	2.4	2.6	1.9
Temperature (°C)	All streams	23.6	22.7	26.1
Antiscalant (mg/L)	Concentrate in stream	48	54	62
Run time (h)		330	138	8

Table 5
Water composition for Experiment #1

	Feed (n = 8)			Product (n = 8)			Concentrate (n = 16)		
Concentration (mg/L)	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max
Ca^{2+}	500	548	576	254	282	350	2,988	3,442	4,360
Mg^{2+}	326	360	379	179	199	237	1,667	1,938	2,355
Na^+	793	841	909	648	713	853	1,930	2,201	2,860
Cl^-	523	549	577	367	397	411	1,780	1,893	2,220
SO_4^{2-}	2,900	3,231	3,600	1,770	2,014	2,210	14,300	16,388	20,900
HCO_3^-	295	297	298	262	265	272	366	544	634
NO_3^-	34	36	37	19	20	24	111	138	370
SiO_2	21	22	25	21	23	29	20	24	37
pH	7.3	7.5	7.6	7.2	7.4	7.5	6.6	6.9	7.1
Conductivity (μS/cm)	6,540	6,573	6,660	4,490	4,614	4,710	20,300	21,063	22,800
TDS (mg/L)	5,409	5,898	6,303	3,653	3,922	4,225	24,491	26,653	32,858
Temperature (°C)	23.0	23.6	24.1	23.0	23.6	24.1	23.0	23.6	24.2
SI($CaSO_4$)	0.86	0.97	1.07	0.41	0.45	0.53	7.34	8.16	9.97

Note: n = number of samples analyzed.

during 138 h of continuous operation with 54 ppm antiscalant dosing.

In this experiment, the maximum SI($CaSO_4$) value of 13.20 is significantly higher than the average and may point to system instability. However, this value is close to 3 standard deviations away from the average SI($CaSO_4$) value, and the sample corresponding to this maximum value was consistently high in all of the reported ionic concentrations. Since the operating conditions were very stable throughout the run, it is logical to assume that this measurement value was primarily due to a sampling error and was not a result of system performance.

The system's overall stable operation was confirmed by monitoring for a constant electric voltage and current, and through a visual inspection of the stack, which showed that no scaling had occurred. The experiment was determined to be successfully operated at an average SI($CaSO_4$) of 8.79 and a maximum value of 13.20[1] at the end of the polarity reversal period, with no signs of scaling or performance decline.

3.1.3. Experiment #3

Experiment #3 was the only experiment to encounter catastrophic scaling, which occurred in the

---

[1] This value is uncertain, as it may have resulted from sampling error.

Table 6
Water composition for Experiment #2

	Feed (n = 6)			Product (n = 6)			Concentrate (n = 12)		
Concentration (mg/L)	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max
Ca^{2+}	500	509	516	209	248	267	3,080	3,734	4,960
Mg^{2+}	328	335	343	161	188	201	1,699	2,078	2,892
Na^{+}	757	777	789	631	661	691	1,790	2,028	2,730
Cl^{-}	535	539	545	229	366	413	1,760	1,923	2,040
SO_4^{2-}	2,780	2,905	3,000	1,520	1,722	1,860	13,100	16,108	23,300
HCO_3^-	300	301	303	266	271	275	305	525	671
NO_3^-	34	35	35	21	22	24	118	127	132
SiO_2	22	22	23	23	23	23	23	24	31
pH	6.8	6.9	7.0	6.7	6.8	6.9	5.8	6.3	6.7
Conductivity (μS/cm)	6,300	6,313	6,330	4,520	4,560	4,590	20,200	22,140	29,100
TDS (mg/L)	5,275	5,436	5,553	3,207	3,507	3,744	22,079	26,637	36,785
Temperature (℃)	22.2	22.8	23.4	22.2	22.8	23.4	22.2	22.7	23.5
SI($CaSO_4$)	0.83	0.87	0.88	0.30	0.37	0.41	6.84	8.79	13.20

Note: n = number of samples.

hydraulic system. Within nine hours of start-up, the system automatically shut down due to low pressure in the concentrate recycle loop. No samples were collected for water analysis, due to the unexpected scaling event, and the experimental SI($CaSO_4$) value was estimated as explained below.

The estimated chemical composition of the concentrate streams in Experiment #3 is given in Table 7. This estimate is based on two different methods: (1) a water-sample analysis collected in a previous experiment at a conductivity of 24,500 μS/cm and (2) linear interpolation of "Ionic Concentrations vs. Conductivity" from all the previous data. These estimates were in close agreement with the analysis of the previous experiment's 24,500 μS/cm sample estimating SI ($CaSO_4$) = 10.56 and linear interpolation estimating SI ($CaSO_4$) = 10.34.

The estimated water analyses show that an average SI($CaSO_4$) value of 10.34–10.56 was achieved at the end of polarity reversal periods in the concentrate stream during the 8 h of operation, with 62 ppm antiscalant dosing.

This experiment was determined to be the point of failure for the system. However, the visual inspection of the stack revealed that no scaling had occurred on the membrane surfaces. An inspection of the system hydraulics, however, revealed the cause of the system's automatic shutdown: The entirety of the hydraulic system was coated in approximately 0.3 cm of solid white precipitate, which had disabled the concentrate pump. The precipitate was not reactive to numerous HCl baths. Based on previous experience and the feedwater chemistry, it was determined that calcium sulfate had precipitated, either homo- or heterogeneously.

Table 7
Water composition for Experiment #3

	Concentrate	
Concentration (mg/L)	(1)	(2)
Ca^{2+}	4,200	4,154
Mg^{2+}	2,330	2,326
Na^{+}	2,390	2,461
Cl^{-}	2,490	2,241
SO_4^{2-}	19,200	18,850
HCO_3^-	720	609
NO_3^-	152	153
SiO_2	22	28
pH	–	–
Conductivity (μS/cm)	25,000	25,000
TDS (mg/L)	31,600	30,925
Temperature (℃)	23.0	23
SI	10.56	10.34

Overall, the results indicate that EDR has enormous potential for treating calcium sulfate-rich inland brackish waters. The outcome of the second experiment was particularly promising, with the system successfully operating at an average SI($CaSO_4$) of 8.79 and a maximum value of 13.20[2] at the end of the polarity reversal period. Such operation could significantly reduce the volume of concentrate produced

---

[2] This value is somewhat uncertain, as it may have resulted from sampling error.

from brackish feedwaters and RO concentrate. When operating at an SI($CaSO_4$) of 8.79 in the concentrate stream, recoveries greater than 90% could be achieved when treating feedwaters that are already saturated with calcium sulfate, like many of the waters listed in Table 2.

However, it is important to note that the conductivity of the product water in each experiment is still very high. Since potable water has conductivity less than 800 μS/cm, the product water from these experiments would require additional treatment. Not only does this mean that the achieved experimental recovery ratios cannot be determined simply by using the feed and product flow rates, but it also introduces an element of uncertainty about the general applicability of the system's hydrodynamic/electrochemical conditions.

In scenarios where a greater degree of desalination would be required for the production of potable water, it is likely that the hydrodynamic/electrochemical behavior of the system would become increasingly unfavorable as the degree of desalination is increased. This would result from the combined presence of the hydrodynamic boundary layer, caused by viscous forces, and the concentration boundary layer, caused by mass transfer rates through the membranes. As the degree of desalination is increased within the stack, precipitation is more likely within the hydrodynamic/concentration boundary layer, where the most saline volume of solution is moving at the lowest velocity. Although the residence time of the system would remain approximately the same, the induction time of scaling salts would decrease due to their relatively high concentrations at the membrane surface. For the system to remain operational, the antiscalant would be required to inhibit precipitation to a greater degree, which is further complicated by the tendency of the hydrodynamic boundary layer to hinder mixing.

With all this in mind, the results from Experiment #3 are particularly interesting. The catastrophic failure encountered during this experiment can provide some interesting insight into the hydrodynamic/electrochemical behavior of the system. As indicated in the results, the scaling event thoroughly disabled the concentrate recycle hydraulic system, but did not lead to membrane precipitation. In light of the analysis on the combined presence of hydraulic and concentration boundary layers, the result of Experiment #3 may indicate that the hydrodynamic/electrochemical potential of the EDR stack is greater than that of the hydraulic pipes carrying the concentrate stream. As both the EDR stack and the concentrate recycle hydraulic pipes experience the same water chemistry, there is some evidence that the turbulence-promoting spacers are effectively disrupting the laminar boundary layer next to the membrane surfaces, while in the tubes, the only source of turbulence is fluid velocity. This argument is further strengthened by considering the concentration gradient that is present within the EDR system due to mass transfer through the membranes, but absent from the hydraulic pipes.

The efficiency of the turbulence-promoting spacers may allow the system to operate at even higher SI ($CaSO_4$) values, and possibly at higher degrees of salt removal. The system has demonstrated a very high potential for treating $CaSO_4$-rich brackish groundwaters and could lead to significant reductions in the cost of inland desalination.

4. Conclusion

In order to reduce the prohibitively high cost of inland desalination, there has been a surge of interest in emerging technologies and techniques for recovery enhancement and concentrate minimization. EDR has been identified for its enormous potential as a high-recovery desalination technology, due to its favorable hydrodynamic/electrochemical behavior and polarity reversal feature. The objective of this research was to investigate the performance limitations of pilot-scale EDR for treating calcium sulfate-rich brackish groundwaters, using an advanced antiscalant.

This research was based on the hypothesis that EDR could effectively treat brackish groundwaters with high calcium sulfate concentrations, demonstrating EDR's high-recovery potential for inland brackish water desalination. Through weeks of continuous testing, the hypothesis was confirmed. The pilot-scale EDR system demonstrated the ability to safely and efficiently treat a feedwater that was nearly saturated with calcium sulfate. The highest average SI($CaSO_4$) value achieved during long-term operation, 8.79, is significantly higher than any previously published value for an RO system and demonstrates the high-recovery potential of EDR technology.

Acknowledgments

This research project was partially sponsored by the US Bureau of Reclamation and Office of Naval Research.

Symbols

A — constant
a — anionic species
a'' — anionic species
B — constant
c — cation species
c'' — cation species
C_C — antiscalant dose to the EDR concentrate
C_F — predicted antiscalant dose to the RO feed stream
I — ionic strength
K_{SP} — thermodynamic solubility product
Q_C — flow rate of concrete streams
Q_F — flow rate of feed
Q_P — flow rate of product
R — system recovery
R — universal gas content
T — absolute temperature of solution
X — cationic species
Y — anionic species

Greek

α_i — activity of species i
c_i — concentration of species i
γ_i — activity coefficient
z_i — charge of species of i
$\Delta_f G^{\Phi}$ — Gibbs free energy of formation
$\Delta_r G^{\Phi}$ — standard molar Gibbs free energy of reaction
$\Delta_r H$ — change in enthalpy of reaction

References

[1] D.F. Lawler, M. Cobb, B. Freeman, L.F. Greenlee, K. Katz, W.S. Walker, Improving Recovery: A Concentrate Management Strategy for Inland Desalination, Texas Water Development Board, Austin, TX, 2010.

[2] S. Kalaswad, B. Christian, R. Petrossian, The Future of Desalination in Texas (Volume 2): Technical Papers, Case Studies, and Desalination Technology Resources, Chapter: Brackish Groundwater in Texas, Texas Water Development Board, Austin, TX, 2004.

[3] S.E. Reynolds, Twenty-fifth Biennial Report of the State Engineer of New Mexico for the 49th and 50th Fiscal Years July 1 1960, to June 30, 1962, Valliant Company, Albuquerque, NM, 1962.

[4] T.M. Whitworth, Desalting of saline waters—Applications to New Mexico, New Mex. Geol. 25 (2003) 16–20.

[5] P.V. Brady, R.J. Kottenstette, T.M. Mayer, M.M. Hightower, Inland desalination: Challenges and research needs, J. Contemp. Water Res. Educ. 132 (2005) 46–51, doi: 10.1111/j.1936-704X.2005.mp132001007.x.

[6] P. Malmrose, J. Losier, M. Mickley, R. Reiss, J. Russel, J. Schaefer, Committee report: Current perspectives on residuals management for desalting membranes, J. AWWA. 96 (2004) 73–87.

[7] J.P. Nicot, A.H. Chowdhury, Disposal of brackish water concentrate into depleted oil and gas fields: A Texas study, Desalination 181 (2005) 61–74, doi: 10.1016/j.desal.2005.02.013.

[8] I. Watson, O. Morin, L. Henthorne, Desalting Handbook for Planners, third ed., Report to United States Department of the Interior Bureau of Reclamation, Denver, CO, 2003.

[9] M. Jefferies, D. Comstock, Predicting calculating scaling tendency in membrane plants, Desalination 139 (2001) 341–344.

[10] M. Uchymiak, E. Lyster, J. Glater, Y. Cohen, Kinetics of gypsum crystal growth on a reverse osmosis membrane, J. Membr. Sci. 314 (2008) 163–172, doi: 10.1016/j.memsci.2008.01.041.

[11] C.J. Gabelich, M.D. Williams, A. Rahardianto, J.C. Franklin, Y. Cohen, High-recovery reverse osmosis desalination using intermediate chemical demineralization, J. Membr. Sci. 301 (2007) 131–141, doi: 10.1016/j.memsci.2007.06.007.

[12] L. Bazinet, M. Araya-Farias, Electrodialysis of calcium and carbonate high concentration solutions and impact on composition in cations of membrane fouling, J. Colloid Interface Sci. 286 (2005) 639–646, doi: 10.1016/j.jcis.2005.01.085.

[13] S. Sethi, P. Xu, J. Drewes, New Desalination Configurations and Technologies for Recovery Increase and Concentrate Minimization, in: K.C. Kabbes (Ed.), Restoring Our Natural Habitat Proc. World Environ. Water Resour. Congr. 2007, American Society of Civil Engineers, Tampa, FL, 2007, pp. 1–9.

[14] S. Walker, Improving Recovery in Reverse Osmosis Desalination of Inland Brackish Groundwaters via Electrodialysis, University of Texas at Austin, Austin, 2010.

[15] E. Akyol, M. Öner, E. Barouda, K.D. Demadis, Systematic structural determinants of the effects of tetraphosphonates on gypsum crystallization, Cryst. Growth Des. 9 (2009) 5145–5154, doi: 10.1021/cg9005423.

[16] D. Elyanow, R.G. Parent, J.R. Mahoney, Parametric tests of an electrodialysis reversal(EDR) system with aliphatic anion membranes, Desalination 38 (1981) 549–565.

[17] E. Korngold, L. Aronov, N. Daltrophe, Electrodialysis of brine solutions discharged from an RO plant, Desalination 242 (2009) 215–227, doi: 10.1016/j.desal.2008.04.008.

[18] P. Murray (Ed.), Electrodialysis and Electrodialysis Reversal, first ed., American Water Works Association, Denver, CO, 1995.

[19] M. Turek, P. Dydo, Electrodialysis reversal of calcium sulphate and calcium carbonate supersaturated solution, Desalination 158 (2003) 91–94.

[20] Y. Oren, E. Korngold, N. Daltrophe, R. Messalem, Y. Volkman, L. Aronov, M. Weismann, N. Bouriakov, P. Glueckstern, J. Gilron, Pilot studies on high recovery BWRO-EDR for near zero liquid discharge approach, Desalination 261 (2010) 321–330, doi: 10.1016/j.desal.2010.06.010.

[21] E. Lyster, M. Kim, J. Au, Y. Cohen, A method for evaluating antiscalant retardation of crystal nucleation and growth on RO membranes, J. Membr. Sci. 364 (2010) 122–131, doi: 10.1016/j.memsci.2010.08.020.

[22] A. Rahardianto, J. Gao, C.J. Gabelich, M.D. Williams, Y. Cohen, High recovery membrane desalting of

low-salinity brackish water: Integration of accelerated precipitation softening with membrane RO, J. Membr. Sci. 289 (2007) 123–137, doi: 10.1016/j.memsci.2006.11.043.

[23] Y. Cohen, Membrane Desalination of Agricultural Drainage Water: Water Recovery Enhancement and Brine Minimization, Report to UC Water Resources Center, Riverside, CA, 2008.

[24] A. Wiesner, G. Juby, A. Zacheis, R. Morquecho, T. Mulvihill, Electrodialysis Reversal Provides Effective Treatment Approach for Concentrating Reverse Osmosis Brine, Proc. Water Environ. Fed. WEFTEC 2010, Water Environment Federation, New Orleans, LA, 2010, pp. 2078–2092.

[25] J.E. Miller, Review of Water Resources and Desalination Technologies, Sandia National Laboratories, Albuquerque, NM, 2003.

[26] B.C. McCool, A. Rahardianto, J. Faria, K. Kovac, D. Lara, Y. Cohen, Feasibility of reverse osmosis desalination of brackish agricultural drainage water in the San Joaquin Valley, Desalination 261 (2010) 240–250, doi: 10.1016/j.desal.2010.05.031.

[27] L. Karimi, L. Abkar, M. Aghajan, A. Ghassemi, Study of Technical Feasibility of PV-EDR and PV-RO Desalination in Remote Rural Areas in New Mexico, World Environ. Water Resour. Congr., Portland, Oregan, 2014.

[28] M. Turek, J. Was, P. Dydo, Brackish water desalination in RO–single pass EDR system, Desalin. Water Treat. 7 (2009) 263–266, doi: 10.5004/dwt.2009.710.

[29] C.Martinetti, A.Childress, T.Cath, High recovery of concentrated RO brines using forward osmosis and membrane distillation, J. Membr. Sci. 331 (2009) 31–39, doi: 10.1016/j.memsci.2009.01.003.

[30] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: Water sources, technology, and today's challenges, Water Res. 43 (2009) 2317–2348, doi: 10.1016/j.watres.2009.03.010.

[31] M. Al-Shammiri, M. Safar, M. Al-Dawas, Evaluation of two different antiscalants in real operation at the Doha research plant, Desalination 128 (2000) 1–16, doi: 10.1016/S0011-9164(00)00019-9.

[32] K.S. Pitzer, J.J. Kim, Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes, J. Am. Chem. Soc. 1426 (1974) 5701–5707.

[33] C. Harvie, N. Møller, J. Weare, The prediction of mineral solubilities in natural waters: The Na–K–Mg–Ca–H–Cl–SO_4–OH–HCO_3–CO_3–CO_2–H_2O system to high ionic strengths at 25°C, Geochim. Cosmochim. Acta 48 (1984) 723–751, doi: 10.1016/0016-7037(84)90098-X.