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Development of a Treatment Process for Electrodialysis Reversal Concentrate with Intermediate Softening and Secondary Reverse Osmosis to Approach 98-Percent Water Recovery

Victor F. Medina, M.ASCE[1]; Jared L. Johnson[2]; Scott A. Waisner[3]; Roy Wade[4]; and Jose Mattei-Sosa[5]

Abstract: The United States Army is constructing a new water-treatment facility for Fort Irwin/National Training Center in the Mojave Desert region of southern California to address existing regulatory requirements and to account for anticipated expansion at the installation. The proposed treatment, electrodialysis reversal (EDR), is anticipated to recover 92% of the influent water. The ultimate goal was to achieve 99% recovery, which required additional recovery of the EDR concentrate. This paper describes laboratory testing of conventional water-treatment methods to achieve water recovery beyond standard practice. The effectiveness of lime softening followed by secondary reverse osmosis (RO) was evaluated to treat the concentrate stream and recover additional water to approach 98%. Partial lime softening at dosages of $500 - 2,000$ mg/L of hydrated lime was capable of removing hardness from simulated EDR concentrate. Adding magnesium chloride to the lime softening step increased silica removal, bringing SiO_2 concentrations in the simulated EDR concentrate from 110 to 6.8 mg/L at room temperature. The resulting treated water was suitable for effective reverse osmosis with a standard seawater polyamide membrane. Rejection for all of the dissolved constituents was well above 90% with the exception of arsenic, which was reduced from 50 μg/L to levels on the order of 20 μg/L. To achieve 99% recovery, mechanical vapor recompression is being considered to further recover the concentrate from the RO unit, although this unit process was not evaluated in the research reported in this paper. **DOI: [10.1061/(ASCE)EE.1943-7870.0000929](https://doi.org/10.1061/(ASCE)EE.1943-7870.0000929).** © 2015 American Society of Civil Engineers.

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Introduction

The United States Army is constructing a new water-treatment facility for Fort Irwin/National Training Center in the Mojave Desert region of southern California [Government Services Administration (GSA 2012)]. Source water at the site is a mix of groundwater basins averaging 520 mg/L of total dissolved solids (TDS). The blended groundwater also contains 5 mg/L of fluoride and 14 μg/L of arsenic (Fort 2011). These levels necessitate a treatment approach to meet the California maximum contaminant levels (MCLs) of 2 mg/L for fluoride and 10 μg/L for arsenic (California Department of Public Health 2008).

Total silica concentrations in the groundwater approach 80 mg/L, which can foul reverse osmosis (RO) membranes (Sheikholeslami et al. 2001; Ning et al. 2010). Consequently, electrodialysis reversal (EDR) was chosen as the primary water-treatment process because this process can provide effective treatment of the constituents of interest while avoiding issues associated with silica fouling. A pilot test of EDR indicated that a two-stage system could reliably obtain 92% water recovery while meeting all other treatment goals (CH2M Hill 2007).

Fort Irwin is located in an arid region with limited groundwater recharge. Sustainability assessments have demonstrated that existing water resources at Fort Irwin are stretched, and exploiting new water sources would be both cost-prohibitive and legally difficult (Jenicek et al. 2011). In order to maintain the mission effectiveness and sustainability of Fort Irwin, very high recovery water treatment is a necessity. Although it has not ever been accomplished on this scale in the literature (Table 1), an ambitious recovery goal of 99% was targeted by the Fort Irwin management. This required recovery of water in the EDR concentrate.

A design for a 6-million gal./day (mgd), i.e., 22,740 m^3/day, plant was developed to accomplish the goal of 99% recovery (CH2M Hill 2007; Fig. 1). The EDR will be used to treat the influent water. The EDR concentrate will then be treated with a combination of lime softening (which includes filtration, acidic pH adjustment, and air stripping) and reverse osmosis. The purpose of the lime softening was to reduce silica to limit fouling of the RO

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Table 1. Summary of High Water Recovery Systems for High TDS Water Sources Reported in the Literature

Reference	Location	Scale	Technology[a]	Recovery (%)	Application
Argo (1984)	California, United States	Pilot plant	Lime and RO	Not reported	Wastewater
Lee et al. (2009)	Singapore	Benchtop	RO and CDI	85	Industrial wastewater
Harries et al. (1991)	Canada	Pilot plant	RO and EDR	75/85	Brackish groundwater
Karahawa (1994)	Japan	Full scale	ED	86	Seawater
Korngold et al. (2009)	Israel	Pilot plant	RO and EDR	97–98	Brackish groundwater
Lozier et al. (2006)	Big Bear Valley, California, United States	Computational study	RO and EDR	79	Brackish water source
Carollo Engineers (2005)	Sarasota County, Florida, United States	Full scale	EDR	85	Brackish groundwater
GE (2009)	Magna, Utah, United States	Full scale	EDR	Not reported	Arsenic-containing groundwater
GE (2008)	Suffolk, Virginia, United States	Full scale	EDR	94	Fluoride-containing groundwater
Valero et al. (2011)	Barcelona, Spain	Full scale	EDR	90	Brackish surface water
Ebadirad (personal communication, 2011)	Yuma, Arizona, United States	Full scale	EDR	94–95	Groundwater

Note: Adapted from Medina et al. (2012).
[a]CDI = capacitive deionization; ED = electrodialysis; and Lime = lime softening.
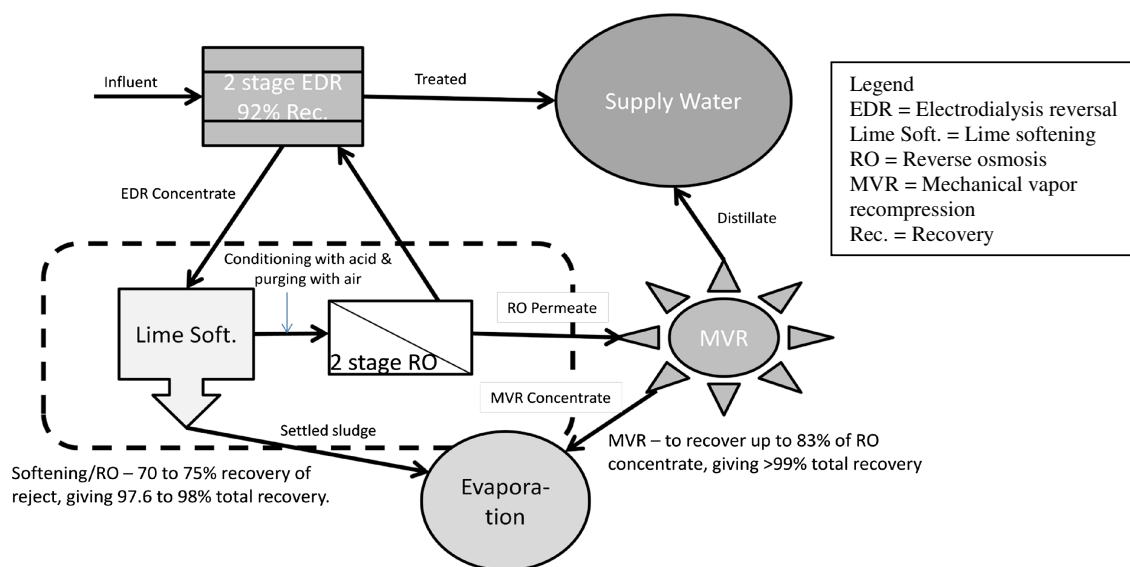
Fig. 1. Proposed process flow diagram for Fort Irwin water-treatment plant; lime soft = lime softening (with filtration and pH adjustment); MVR = mechanical vapor recompression

membrane. It was projected that this combination would recover 75% of the concentrate, resulting in a total water recovery of 97–98%. The design planned for the RO permeate to return to the EDR system to ensure reduction of arsenic to potable water standards. To meet the 99% recovery goal, mechanical vapor recompression (MVR) was planned to recover an additional portion (just over 80%) of the RO concentrate. It is likely that the full-scale plant will resemble this plan but there could be significant changes by the engineering/construction contractor (GSA 2012) such as the use of alternative technologies, i.e., electrocoagulation instead of conventional softening (Medina et al. 2013).

The scope of the treatment requirements are ambitious and will place Fort Irwin at the leading edge of what is currently feasible for municipal water supply in extremely arid regions. High recovery and zero liquid discharge (ZLD) technologies have been investigated and tested at pilot scale for several years, although the costs for implementing these approaches remain prohibitively high (Mickley 2008). Efforts are ongoing to increase the efficiency of secondary membrane processes to treat reject brines with major points of focus being appropriate intermediate treatment

technologies and improved process controls, to mitigate membrane fouling and scaling from highly concentrated brines. For the anticipated reject from Fort Irwin the main scaling concerns will be divalent cations of calcium and magnesium, and silica. One approach to handling silica in an RO system is the aggressive use of antiscalants, which facilitates very high recovery in silica-dominated brine treatment (Ning et al. 2010). Hardness is also a concern for reject treatment at Fort Irwin, so an intermediate precipitation step would be an appropriate way to improve the treatability of the reject by secondary RO. In systems where hardness ions and silica are a concern, intermediate precipitation is effective using lime softening in conjunction with magnesium hydroxide precipitation of silica (Ning et al. 2006). Gabelich et al. (2007) effectively removed hardness ions from Colorado River water by alkaline (NaOH) softening with a lesser removal of silica by coprecipitation in a solids contact clarifier. Other intermediate precipitation approaches have included fluidized bed crystallization (Bond 2008), selective precipitation by separate lime and soda ash processes for resource recovery (Mohammadesmaeili et al. 2010), and partial lime softening followed by ion exchange (Comstock et al. 2011). A pilot

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demonstration of primary RO followed by caustic soda precipitation and secondary RO was able to achieve 95% recovery of Colorado River water over a 550-h treatment run (Gabelich et al. 2011). Insufficient information exists for the (to the best of the writers' knowledge) relatively rare case of a primary EDR treatment followed by RO concentration of the reject.

The goal of the research reported in this paper was to evaluate the effectiveness of common-practice treatment methods that could be applied to the anticipated EDR concentrate to achieve results that exceed common-practice design, improving the water recovery of the system from 92 to 97% or higher. To accomplish this, a combination of lime softening followed by secondary RO treatment of EDR concentrate was studied. The performance of partial lime softening for the treatment of simulated EDR concentrate was observed using standard jar tests. This process was built on by further testing of partial lime softening with added magnesium chloride for silica precipitation. The resulting water was treated by secondary RO for process evaluation.

Methods

Simulated EDR Concentrate

Pilot testing of a single-stage EDR unit along with process modeling provided the expected chemical composition of concentrate from a three-stage EDR treatment system (CH2M HILL 2007) as detailed in Table 2. The EDR treatment is expected to operate with 92% recovery with a concentration factor for charged constituents of about 10. Because it is not a charged species, minimal accumulation of total silica in the EDR concentrate was assumed, although depending on the current density, charge splitting can occur at the membrane solution interface, resulting in some transfer into the concentrate. Table 3 summarizes the chemicals and amounts used to prepare a 20-L batch of simulated EDR concentrate. This formulation was used as the starting point for all of the intermediate softening tests. Chemicals were added in dry form, the pH was adjusted to 8.3 with 3 N nitric acid, and the system was left to fully equilibrate overnight.

Table 2. Expected Three-Stage EDR Concentrate Constituents for Fort Irwin Water-Treatment Plant

Constituent	Units	Source water	Electrodialysis reversal concentrate	Finished water goal
pH	pH units	8.0	8.2–8.3	7–8
Arsenic, As	$\mu g/L$	30	50	7.5
Barium, Ba^{2+}	mg/L	0.031	0.3–0.4	—
Bicarbonate	mg $CaCO_3/L$	133	1,600–1,700	—
Chloride, Cl^-	mg/L	92	1,000–1,100	—
Calcium, Ca^{2+}	mg/L	23	200–300	—
Fluoride, F^-	mg/L	5.4	63–65	1.6
Magnesium, Mg^{2+}	mg/L	3	30–35	—
Total silica, SiO_2	mg/L	76	80–90	—
Sodium, Na^+	—		Not given	
Strontium, Sr^{2+}	mg/L	0.4	4.5–4.6	—
Sulfate, SO_4^{2-}	mg/L	153	1,300–1,400	—
Total dissolved solids	mg/L	583	6,400–6,500	500–1,000
Hardness	mg $CaCO_3/L$	70	820–850	—

Note: Adapted from CH2M Hill (2007).

Intermediate Softening Studies

Jar testing was conducted using a Phipps and Bird jar test apparatus (Hammer 1986; Reynolds 1977) for automated repeatable flash mixing/settling tests. The first experimental phase evaluated partial lime softening using hydrated lime (98% purity, Falco Lime, Vicksburg, Mississippi). The second experimental phase incorporated magnesium chloride ($MgCl_2$) into lime softening to enhance silica precipitation with magnesium hydroxide. During jar testing preweighed amounts of dry lime were flash mixed into 1 L of simulated EDR concentrate at 100 revolutions/min for 1 min, then a flocculation period of 5 min at 60 revolutions/min was allowed, and a 45-min period of quiescent settling [based on Wade (1988)]. After settling, samples were collected at the 750-mL level from each container for physical and chemical analyses. If $MgCl_2$ was added for additional precipitation, then a preweighed dry powder was added at the same time as lime addition. A no-added-chemical control was included with each set of jar tests. Treatment temperatures were varied from 20.5 to 47°C by conducting testing in a temperature-controlled environmental chamber.

Reverse Osmosis

Reverse osmosis testing was conducted using an Osmonics benchtop unit, which is designed for laboratory research studies on RO processes (Sterlitech Corporation, Kent, Washington). This aspect of the research reported in this paper was conducted with a standard seawater polyamide membrane (AD series, GE Water and Process Technologies, Trevose, Pennsylvania). The areal dimensions of the membrane were 190×140 mm and its thickness was 7 mils (0.1778 mm). The system was operated in cross-flow mode.

The influent of the RO operation was softened EDR simulant based on the results of jar testing. Simulated EDR concentrate (prepared in accordance with Table 3) was treated with 1,500 mg/L $Ca(OH)_2$ and 750 mg/L $MgCl_2$ as described in the previous section. Softened concentrate was filtered by 0.45-μm cartridge filter, then adjusted to pH 5.7 by 1 N hydrochloric acid (HCl) and sparged with compressed air for 12 h. This solution was treated by the RO unit. Target fluxes ranging from 4–12 gal./ft^2/day (163–488 L/m^3/day) were tested at target permeate recoveries ranging from 40–70%.

Analytical

Samples from the processing steps were analyzed for common water quality parameters. Total suspended solids (TSS) and total dissolved solids were determined gravimetrically by EPA Method 160.1 (U.S. EPA 1999). Anionic and cationic constituents were measured by ion chromatography with conductivity detection

Table 3. Electrodialysis Reversal Concentrate Simulant Formulation in 20-L Batch

Chemical name	Chemical formula	Chemical mass added (g)
Sodium arsenite	$NaAsO_2$	0.0154
Sodium silicate	$Na_2O_3Si \cdot 9H_2O$	17.88
Magnesium chloride	$MgCl_2$	2.54
Strontium chloride	$SrCl_2$	0.1646
Sodium sulfate	Na_2SO_4	22.18
Sodium chloride	NaCl	31.36
Sodium fluoride	NaF	2.82
Sodium bicarbonate	$NaHCO_3$	41.16
Barium sulfate	$BaCl_2$	0.0106
Calcium sulfate	$CaSO_4 \cdot 2H_2O$	21.47

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[EPA Method 300.1 (U.S. EPA 1993)]. Hardness was calculated using the sum of calcium and magnesium concentrations. Total arsenic and total silicon concentrations were determined by inductively coupled plasma (ICP) atomic emission spectroscopy (AES) as per EPA Method 200.7 (U.S. EPA 1994), with silicon being reported as silica (SiO_2). Because the treatment methods are well-established and are considered to be readily predictable, this aspect of the research reported in this paper did not incorporate replication as part of its design.

Results

Partial Lime Softening

Table 4 gives the treatment goals for the lime softening unit process. The effect of hydrated lime dosage on TSS, TDS, turbidity, total silicon (as SiO_2), and hardness is shown in Fig. 2. The pH increased with lime dosage, from 8.7 to 11.9. Alkalinity also increased, from 250 to 850 mg $CaCO_3/L$, as the lime dosage increased. A goal of the lime softening process was to reduce calcium and hardness levels, to protect the RO unit from scaling (Table 4). Lime dosages of 10 mg/L or less did not affect calcium or hardness levels. However, treatments of 200 mg/L began to show modest decreases of these constituents. At 2,000 mg/L, removal of hardness and calcium were substantial and exceeded the targets established in Table 4 (postfiltration). Silica was a key parameter to remove during the lime softening process because silica can foul RO membranes. Partial lime softening appeared to affect a modest removal of silica, reducing levels from about 111 to 93 mg/L, at a treatment does of 2,000 mg/L. The target of 10 mg/L was not achieved by partial lime softening alone. Although removal of TDS and fluoride were not critical for the lime softening process, some removal was desirable to ease the load on the RO unit. The partial lime softening treatment did not have any appreciable effect on TDS and fluoride levels for the dosages tested.

Reduction of calcium, hardness, and silica were needed to reduce potential scaling/fouling issues in the RO unit. Partial lime softening was effective at removing hardness and calcium, which

Table 4. Water Softening Goals for the Research Reported in This Paper

Constituent	Units	Electrodialysis reversal reject, softening influent	Softening effluent	Postfiltration
Arsenic, As	μg/L	—	—	5.77
Barium, Ba^{2+}	mg/L	0.3–0.4	0.2	0.2
Bicarbonate	mg/L	1,600–1,700	38	391
Calcium, Ca^{2+}	mg/L	200–300	8.5	8.5
Chloride, Cl^-	mg/L	1,000–1,100	1,225	1,225
Fluoride, F^-	mg/L	63–65	44	44
Magnesium, Mg^{2+}	mg/L	30–35	30-35	30–35
Silica, Si	mg/L	80–90	10	10
Sodium, Na^+		No level specified		
Strontium, Sr^{2+}	mg/L	4.5–4.6	2.8	2.8
Sulfate, SO_4^{2-}	mg/L	1,300–1,400	1,300–1,400	1,300–1,400
Hardness	mg as $CaCO_3/L$	820–850	170	170
Total dissolved solids	mg/L	6,400–6,500	6,000–6,300	5,400
pH	pH units	8.2–8.3	10.3	7.0
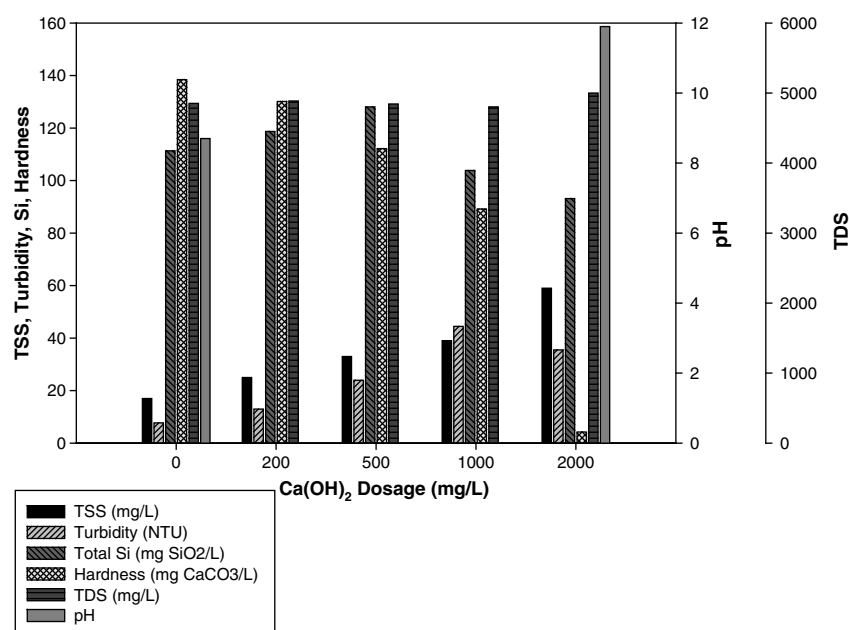
Fig. 2. Effect of partial lime softening on major constituents of a simulated EDR concentrate
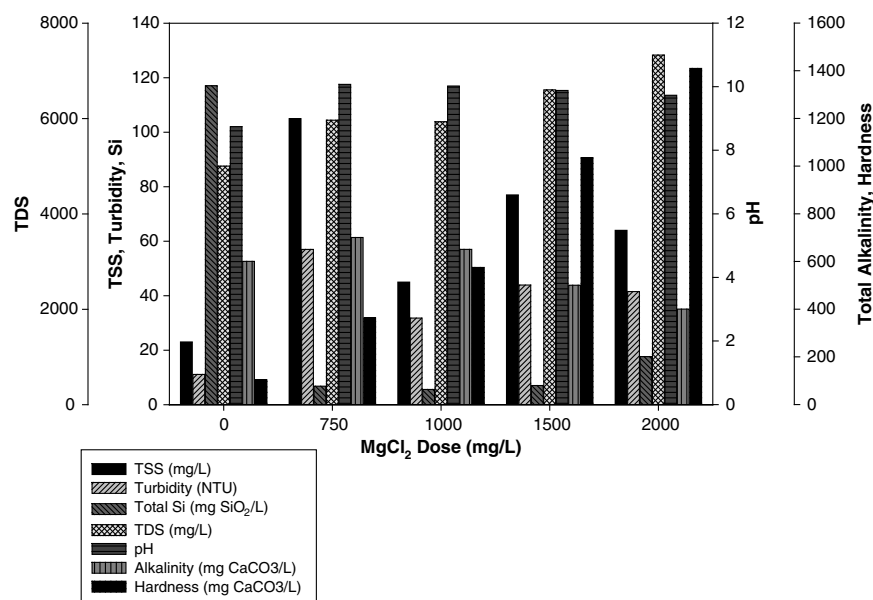
Fig. 3. Effect of added $MgCl_2$ along with $1,500 \text{ mg/L} \, Ca(OH)_2$ for intermediate softening of a simulated EDR concentrate water at room temperature $(25°C)$

was one the goals of the research reported in this paper (Table 4), and removal of these increased as lime dosage increased. Hardness removal was on the order of 59% and calcium removal approached 76%. However, partial lime softening alone was not effective at removing silicon (representing silica). Partial lime softening using only hydrated lime could be an effective pretreatment for the RO system but high silica would require the use of an antiscalant to address silica fouling.

Lime Softening with Magnesium Chloride

Additional silica removal was accomplished by addition of magnesium chloride ($MgCl_2$) to the intermediate softening step. Magnesium chloride hydrates in water to form insoluble magnesium hydroxide [$Mg(OH)_2$] that will coprecipitate silica and other dissolved solids. Based on the results of partial lime softening, a hydrated lime dose of 1,500 mg/L was set, given that 2,000 mg/L appeared to exceed the treatment levels of calcium and hardness, and reducing the lime dosage was considered to be important to keeping operating costs lower. Varying doses of $MgCl_2$ were studied to optimize silica removal. The effect of adding $MgCl_2$ at room temperature on TSS, turbidity, total silicon (expressed as SiO_2), and hardness is shown in Fig. 3. Precipitation with $MgCl_2$ produced an immediate effect on total silicon (representing silica) reducing the observed concentration, from 117 to 6.8 mg/L, at an added dose of 750 mg/L. Total arsenic was reduced from 379 $\mu g/L$ water softened only with 1,500 mg/L hydrated lime, to 77 $\mu g/L$ when 750 mg/L $MgCl_2$ was also added. This dose also affected a reduction in fluoride, from 87.2 to 40.8 mg/L. Compared to partial lime softening with hydrated lime alone, adding $MgCl_2$ increased suspended solids and hardness. At higher doses, the hardness of the treated water was greater than the simulated EDR concentrate water used for testing.

It was hypothesized that magnesium hydration would be strongly affected by temperature, so precipitation experiments at multiple controlled temperatures were undertaken to determine the process characteristics of softening with both hydrated lime and magnesium chloride, particularly since Fort Irwin is in a desert area where elevated temperatures are common. Fig. 4 shows the effect of

increased temperatures on silicon (representing silica) and hardness in simulated EDR concentrate. At all of the observed temperatures, the total hardness of the treated water rose steeply as the added concentration of $MgCl_2$ increased. However, higher treatment temperatures were able to moderate this increase in hardness by delaying the increase to higher $MgCl_2$ dosages, and at a temperature of $47°C$ the sharp increase in total hardness did not occur until the
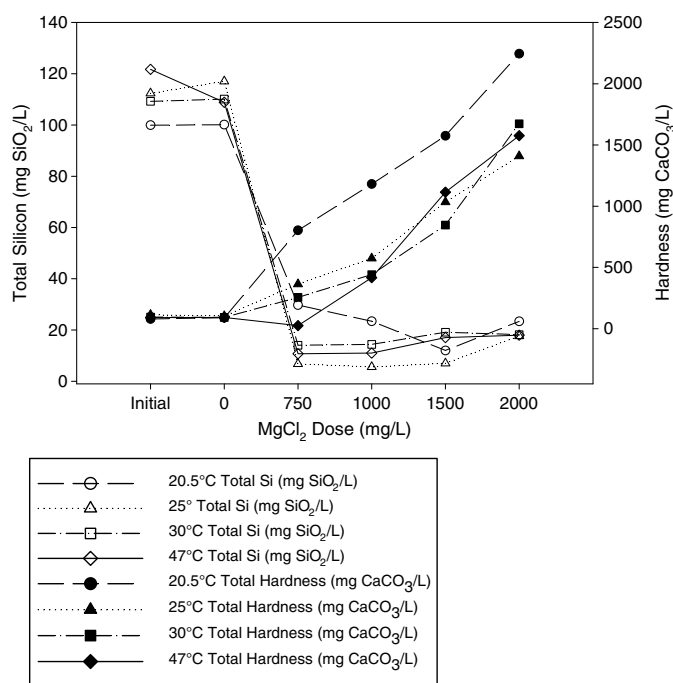
Fig. 4. Total silicon as SiO_2 (open symbols) and hardness as $CaCO_3$ (filled symbols) resulting from addition of varying doses of $MgCl_2$ to 1,500 mg/L hydrated lime softening in a simulated EDR concentrate at controlled temperatures of $20.5°C$ (circles), $25°C$ (triangles), $30°C$ (squares), and $47°C$ (diamonds)
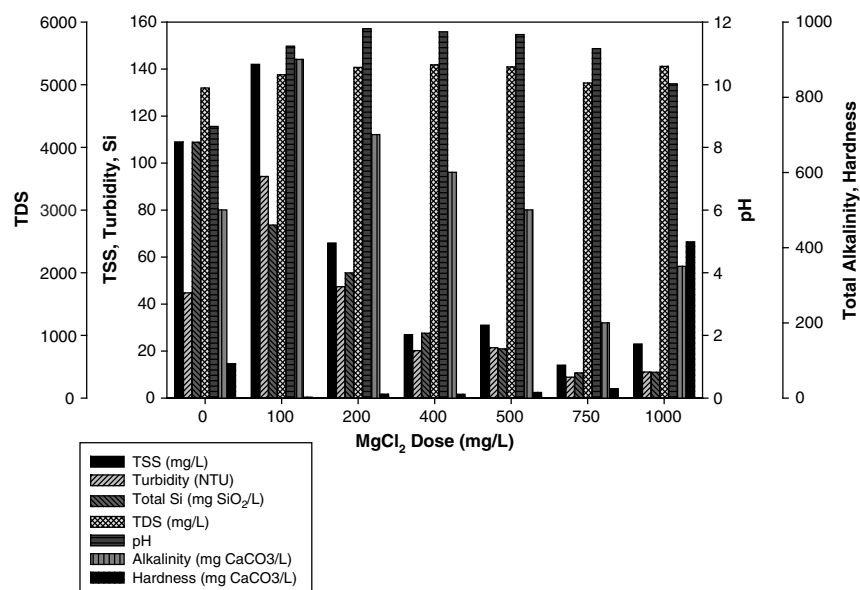
Fig. 5. Effect of added $MgCl_2$ along with 1,500 mg/L $Ca(OH)_2$ for intermediate softening of a simulated EDR concentrate at 47°C

added concentration of $MgCl_2$ exceeded 750 mg/L. The sharp increases were attributable to dissolved magnesium remaining in the water rather than precipitating as hydroxide species. This may be a function of the allowed settling time in the experiments and an increased settling time may reduce total hardness at all temperatures. At an $MgCl_2$ dose of 750 mg/L, all of the treatment temperatures exhibited a rapid decrease in total silicon (representing silica). This removal did not improve with additional $MgCl_2$ dosing. The temperature studies demonstrate that increasing the treatment temperature does not provide especially large improvements in silicon removal but it does reduce the hardness of the treated water by reducing the amount of soluble magnesium remaining in the water.

Since added magnesium chloride above 750 mg/L did not exhibit added silicon (silica) removal, additional settling tests were conducted to observe the effect of lower $MgCl_2$ doses and determine the optimum dose. The observed TSS, turbidity, silicon (representing silica), and hardness for additional settling tests

conducted at 47°C are shown in Fig. 5. Silicon (silica) removal consistently improved as $MgCl_2$ doses from 100 to 750 mg/L were added to the 1,500-mg/L hydrated lime treatment. The total hardness of the treated water increased slightly with higher doses and then markedly increased at the final dose of 1,000 mg/L. Removal efficiency varied from 0.35 mg silicon as SiO_2 removed per mg $MgCl_2$ added at a dose of 100 mg/L, to 0.13 mg silicon as SiO_2/mg $MgCl_2$ at a dose of 750 mg/L.

The chemistry of the simulated EDR concentrate treated by intermediate softening with 1,500 mg/L hydrated lime and 750 mg/L magnesium chloride at each treatment temperature is detailed in Table 5. The intermediate softening step was effective at removing arsenic, fluoride, and calcium. The TDS and chloride increased, which was expected with the addition of magnesium chloride. Hardness and magnesium both increased for the 750 mg/L $MgCl_2$ and 1,500 mg/L $Ca(OH)_2$ treatments at 20.5, 25, and 30°C compared to the untreated simulant (Table 5). The

Table 5. Summary of Water Chemistry Parameters

Analytes	Units	Average EDR reject simulated concentration	Temperature (°C) 20.5	25	30	47
As	mg/L	0.401	0.206	0.080	0.100	0.061
Ca	mg/L	14.4	8.9	10.0	11.7	8.37
Cl	mg/L	1,093	1,606	1,666	1,619	1,661
F	mg/L	79.0	43.8	40.8	34.4	26.4
Mg	mg/L	14.2	108.9	82.2	54.8	1.02
NO_3 ion	mg/L	3.51	<0.5	<0.5	2.31	<0.5
SiO_2	mg/L	110.8	29.7	6.8	14.1	10.7
Na	mg/L	1,302	1,272	1,281	1,265	1,293
Total hardness	mg $CaCO_3$/L	94.4	469	363	255	25.1
Total alkalinity	mg $CaCO_3$/L	893	701	701	550	200
pH	—		10.3	10.1	10.0	11.2
TSS	mg/L	654	105	105	223	14
Turbidity	Nephelometric turbidity units	280	44.6	57.0	47.6	8.88
Total dissolved soilids	mg/L	4,941	5,940	5,964	5,301	5,028

Note: Refers to partial lime softening (hydrated lime concentration of 1,500 mg/L) amended with $MgCl_2$ (750 mg/L) at temperatures ranging from 20.5–47°C.

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increase in dissolved magnesium was greater than 5 times at 20.5°C. Hardness was reduced nearly 75% in the highest temperature tested, 47°C. Alkalinity was reduced with increasing temperature, ranging from over 700 mg $CaCO_3$/L at 20.5°C, to 200 mg $CaCO_3$/L at 47°C. The main apparent difference in the treatments is an increase in dissolved magnesium resulting from inefficient hydration to create insoluble $Mg(OH)_2$ at lower temperatures. One approach to mitigate this inefficient hydration would be to increase the effective settling time of the precipitation process.

Postsoftening Treatment

The $MgCl_2$/lime softening process was effective at removing silica, but resulted in elevated Mg levels and hardness at temperatures ranging from 20.5 to 30 C. At 47°C, removal of these constituents improved to acceptable levels. Although the desert climate at Fort Irwin routinely approaches or exceeds 47°C, temperatures are commonly lower at night or during wintertime. So, postsoftening treatments were explored to address the hardness and Mg levels at the lower temperatures. After intermediate softening the 20.5°C $MgCl_2$/lime-treated water (Table 5) was filtered with a glass fiber cartridge filter (0.45 μm), and the pH adjusted to 5.7 with HCl. Then the alkalinity was rebalanced with atmospheric carbon dioxide by air sparging. These processes greatly modified the softened water, as detailed in Table 6. Dissolved Mg decreased, from 108 mg/L to 18 mg/L (Tables 5 and 6), and hardness decreased 400–100 mg/L as $CaCO_3$. The final pH of the solution was 7.83. The alkalinity was estimated to be 200 mg $CaCO_3$/L. Therefore, with posttreatment the lime-softened water, even at lower temperatures, could meet the requirements for the RO system.

The Langelier saturation index (LSI) measures the potential of water for scaling and corrosion. An LSI < 0 is corrosive and could damage iron pipes. An LSI > 0 can deposit scale. Some scale can be positive as it can provide corrosion protection of pipes. However, too much scale can lead to clogging of pipes, damage to valves, and fouling of the RO membrane. A level between 0 and 0.5 is considered ideal. The LSI was calculated using the method described in Wastewater to be 0.36.

Reduced hardness after neutralization and rebalancing appears to result from the high inorganic carbon content in the EDR simulant. High alkalinity in the EDR concentrate simulant indicates that the bicarbonate/carbonate concentration is substantially greater than that of the magnesium, which favors complexation of the carbonate forms with magnesium. Magnesium carbonate is more soluble than magnesium hydroxide. As a result, at lower temperatures magnesium remained dissolved, contributing to greater hardness. As the alkalinity was reduced during neutralization, the formation of insoluble magnesium hydroxide would be favored.

Table 6. Water Chemistry of RO Influent

Parameter	Value
F (mg/L)	31.2
Cl (mg/L)	1,843
SO_4 (mg/L)	1,277
Ca (mg/L)	10.1
Mg (mg/L)	18.3
As (mg/L)	0.050
SiO_2 (mg/L)	15.2
pH	7.84
Hardness (mg $CaCO_3$/L)	100
Alkalinity (mg $CaCO_3$/L)	<200
Langelier satuation index	0.36
pH	7.83

Sludge Generation Associated with Softening

In addition to being a potential environmental liability, sludge generation for the proposed treatment is important in that it represents a loss of water during the settling process. Table 7 includes sludge generation data for the partial lime treatment (dosage of 1,500 mg/L) with supplementary magnesium chloride (750 mg/L). Percent wet sludge ranged from 2.4 to 3.5%. Using the assumption that the solids have a specific gravity of 1.6, the percentage water lost from magnesium chloride (750 mg/L) supplemented partial lime softening (1,500 mg/L hydrated lime) ranged from 0.08% (at 25°C) to 0.16% (47°C) of the design flow of 6 mgd (22,740 m^3/day). These small losses are acceptable to meet the 99% recovery goal but additional water recovery methods such as a taller clarifier with a thicker sludge blanket, filter press, vacuum filtration, or sludge pond decant recovery and recycle could improve water recovery associated with the partial lime-softening process.

Reverse Osmosis Treatment

The RO studies were conducted with fluxes ranging from just over 122 L/m^3/day (3 gal./ft^2/day) to just under 488 L/m^3/day (12 gal./ft^2/day), and with permeate recoveries ranging from just over 40% to nearly 70% for a single-stage system. At these conditions, operating pressures ranged from just below 120 psi (8.27×10^5 Pa), to just over 270 psi (18.61×10^5 Pa). At a given flux, operating pressures increased as the system was adjusted to achieve a higher permeate recovery.

Table 8 shows RO permeate water chemistry at two flux rates close to 0.41 m/day (10 gal./ft^2/day), with water recoveries of 53 and 56%. Fluoride ranged from 1.65 to 1.90 mg/L, below the MCL of 2 mg/L but still above the treated water goal of 1.6 mg/L. Rejection for all of the dissolved constituents was well above 90% with the exception of arsenic. Arsenic was reduced from 50 μg/L to levels on the order of 20 μg/L, above the treated water goal of 7.5 μg/L and the MCL of 10 μg/L. The lowest observed arsenic concentration was 11 μg/L, at a flux of 0.33 m/day (8.15 gal./ft^2/day) and a recovery of 57.1%. Silica rejection was above 97% but as a result of the intermediate softening step, total silica in the concentrate remained below the solubility of SiO_2 at room temperature [American Water Works Association (AWWA) 2007].

This paper indicates that RO is able to effectively treat the EDR concentrate after an intermediate softening step to meet the project goals. However, drinking water standards were not met due to arsenic. Single-stage operation at 53% recovery was achieved. Assuming that both stages achieve 53% recovery, then a two-stage operation should be able to have a water recovery 78%, i.e., 53% + (47% × 0.53), meeting the recovery goal of 70–75% recovery for RO treatment of the EDR concentrate.

Table 7. Summary of Sludge Properties

Sludge properties	Units	Temperature (°C)			
		20.5	25	30	47
Sludge volume	mL	24	20	30	35
Wet sludge	% v/v	2.4	2.0	3.0	3.5
Solids per volume treated, dry	g/L	0.69	0.45	0.73	1.18
Sludge solids	% w/v	2.9	2.2	2.4	3.4

Note: Refers to partial lime softening (hydrated lime concentration of 1,500 mg/L) amended with $MgCl_2$ (750 mg/L) at temperatures ranging from 20.5 to 47°C.

Table 8. Water Chemistry at Two Flux/Recovery Conditions

Parameter	Influent	Permeate	Permeate	Rejected (%)	Missing (%)
Operating conditions					
Flux [m/d (gfd)]	—	0.40 (9.87)	0.44 (10.77)	—	
Recovery (%)		53.0	56.2		
Pressure (psig)		241	258		
Constituents					
Fluoride (mg/L)	31.2	1.90	1.65	93.9–94.7	—
Chloride (mg/L)	1,843	74	67	96.0–96.4	—
Sulfate (mg/L)	1,277	25.1	18.6	98.0–98.5	14.3–7.9
Calcium (mg/L)	10.1	0.183	0.143	98.2–98.6	—
Magnesium (mg/L)	18.3	0.339	0.197	98.1–98.9	—
Arsenic (mg/L)	0.050	0.020	0.027	60.0–46.0	—
Silica (mg SiO_2/L)	15.2	0.419	0.378	97.2–97.6	—
Barium (mg/L)	—	0.012	0.007	—	—
Hardness (mg/L)	100.7	1.85	1.17	98.2–98.8	—

Discussion

Novel Aspects of the Research Reported in This Paper

The research reported in this paper uses conventional treatment processes, such as $MgCl_2$-modified lime softening and reverse osmosis, to achieve a novel result, i.e., water recovery in excess of 97%. Silica is a key design parameter in high water recovery systems since it can lead to membrane fouling in RO systems. Because of this, many of systems that promote high water recovery use RO as the primary treatment, which concentrates silica as well as other ionic species, followed by electrodialysis reversal, which is not as affected by the silica concentration (Table 1 shows five such examples). However, in this case the source water had unusually high silica concentrations. This required the use of EDR as the primary treatment process. However, since EDR was used as the primary treatment it would have diminishing effectiveness for the concentrate. Reverse osmosis could be effective but would be adversely affected by the high silica concentration. The solution was to add the $MgCl_2$-modified lime softening step. In combination, these treatments successfully met the project criteria.

Arsenic

The testing accomplished drinking water standards for all constituents except for arsenic. This incomplete treatment will require permeate from the RO to go to the headworks of the EDR system, which is part of the system design (Fig. 1).

It is also possible to improve the removal of arsenic by oxidizing the arsenic with hypochlorite as it enters the lime softener, and adding ferric chloride, which will precipitate arsenic as ferric arsenate or the mineral scorodite. This would mean dechlorinating with sodium metabisulfite ahead of the RO units to avoid oxidation damage to the membranes.

Applications to Other Water-Treatment Systems

The research reported in this paper was focused on the groundwater issues found at Fort Irwin. However, the findings are certainly applicable to other groundwater-treatment systems dealing with high dissolved solids and highly stressed water supplies. Membrane technologies are proven processes for the treatment of high TDS water. However, the downside is that a portion of the water is left with high solids, and this portion is typically wasted by evaporation or as a wastewater discharge. Treatment of the concentrate provides the opportunity to achieve water recovery of 95% or higher.

The approach of using membrane processes in tandem appears to be the state-of-the-art for enhanced recovery of water from high TDS source waters (Table 1). Systems have included RO/RO and RO/EDR systems. Electrodialysis reversal was chosen as the primary system because of concerns of silica fouling. The silica in the concentrate coupled with high hardness was a primary reason why the system included the magnesium-modified lime softening step (Ning et al. 2006). This approach would likely be useful for other sites with high silica concerns, and several studies have focused on silica and hardness issues (Bond 2008; Comstock et al. 2011; Gabelich et al. 2007, 2011; Mohammadesmaeili et al. 2010). However, the advantage of enhanced recovery must be balanced with additional costs (discussed in the next section), additional chemical usage, and system complexity.

Costs

The cost for the Fort Irwin plant was awarded at $100.1 million for the 22,740-m^3/day (6-mgd) facility. Water Reuse Association (WRA 2012) estimated average costs for desalination plants on the order of $8.5 million per mgd ($2,237 per m^3/day) capacity, which gives an estimated cost of $51 million for a 2.27×10^4 m^3/day (6-mgd) plant. Most desalination applications do not require high water recovery. Comparing the $51 million to the $100 million actual cost suggests that the high water recovery components in the Fort Irwin plant increase costs on the order of 100%.

Operating costs are also expected to increase appreciably with recovery of the concentrate added to the system. Strathmann (2004) developed estimated costs for electrodialysis, which can also be applied to EDR due to the strong similarity of the processes. Estimating the feed concentration at 0.4 eq/L gives an estimated operating cost of $0.6/$m^3$. For a 2.27×10^4 m^3/day (6-mgd) operation, the annual operating costs of EDR are estimated at $4.8 million. The concentrate recovery will treat 8% of the total influent water, or 1.82×10^3 m^3/day (0.48 mgd). Hamilton (2009) describes a 2.73×10^3 m^3/day (0.72-mgd) plant in Colorado. The plant treated a different source water but it used a $MgCl_2$/lime combination. Estimated annual operating costs were $4.09 million. Since the Hamilton Engineering plant was 33% larger, the costs of the Fort Irwin system can be estimated as $2.74 million. Estimated unit operating costs for reverse osmosis are given in http://www.water-wastewater.com/pages/ro_desc.html#cost. Using these, it can be estimated that the operating costs for RO would be $0.83/$m^3$ for finished water. If 75% recovery is assumed, then the finished water of the RO system for 2.27×10^4 m^3/day (6-mgd) operation is 1.36×10^3 m^3/day (0.36 mgd), which gives an annual operating cost for the RO system to be $4.04 million, and the total annual operating costs of increasing water recovery, from 92 to 98%, is $6.78 million. The MVR will add still additional operating costs, although on a small portion of the water stream.

High recovery and ZLD technologies have been investigated and tested at pilot scale for several years (Greenlee et al. 2009) and in general the costs for implementing these approaches remain prohibitively high (Mickley 2008). In this case, however, Fort Irwin houses important missions for the U.S. Army, including the National Training Center, which provides critical training for units prior to being deployed, and it provides valuable desert terrain to prepare forces for this type of environment. Because it is not possible to duplicate this valuable training area and because the long-term sustainability of water resources in the area demand very high water recovery, meeting this high water recovery goal becomes a cost-effective alternative. As an added benefit, high recovery will

result in substantially smaller evaporative ponds for the wasted water, which is important due to the limited availability of the area in the Fort Irwin cantonment.

Implications for Military Installations

Fort Irwin, being in an arid, desert environment, has groundwater resources that are being depleted; static water levels in one aquifer, Bicycle Lake, have reportedly dropped 80 ft (24 m) since records have been kept. Its mission is growing, meaning that it will have to use its limited water resources to their maximum potential. One means is to maximize water recovery from their water-treatment system. The state of California as a whole has challenging water resource issues (Schroeder et al. 2012) and this high-recovery plant will help to meet that challenge.

Military installations are also facing pressures to develop and use water more efficiently. Base realignment and closure (BRAC) is resulting in fewer but larger military installations, and the remaining installations must be able to meet water needs for increased mission requirements. Climate change may also result in increasing water resource pressures throughout military installations (Scholze 2011). The U.S. Army Net Zero Water program has set a goal of no net water impact within a given watershed. Although the Net Zero Water program is only being demonstrated at specific installations (https://eko.usace.army.mil/public/fa/netzero/), this program will eventually be adapted across all U.S. Army installations (McHugh 2014). Enhanced recovery of concentrate is critical to address limited water resources in arid environments.

Conclusions

The laboratory project of the research reported in this paper was based on a proposed design for a full-scale, 6-mgd (22,740-m^3/day) water-treatment plant at Fort Irwin. Laboratory testing was performed to evaluate two key unit processes [i.e., (1) lime softening, and (2) reverse osmosis], to treat the anticipated concentrate stream from an EDR system at Fort Irwin (California). Properly applied, these two processes appear to be able to able to recover more than 75% of the concentrate stream, which would allow for a total recovery of approximately 98%. The proposed water-treatment system would also include a MVR system (not tested in the research reported in this paper), which should be able to increase the recovery to 99%. The final design of the plant might incorporate significant changes as deemed necessary by the engineering/construction contractor (GSA 2012).

Acknowledgments

References

Argo, D. R. (1984). "Use of lime clarification and reverse osmosis in water reclamation." *J. Water Pollut. Control Fed.*, 56(12), 1238–1246.

AWWA (American Water Works Association). (2007). *Manual of water supply practices–M46 reverse osmosis and nanofiltration*, 2nd Ed., Denver.

Bond, R. (2008). "Zeroing in on ZLD technologies for inland desalination." *J. Am. Water Works Assoc.*, 100(9), 76–89.

California Department of Public Health. (2008). "Maximum contaminant levels and regulatory dates for drinking water: U.S. EPA versus California." ⟨http://www.cdph.ca.gov/certlic/drinkingwater/Documents/DWdocuments/EPAandCDPH-11-28-2008.pdf⟩ (Jul. 19, 2012).

Carollo Engineers. (2005). *Water supply master plan update*, *Technical Memoradum 2*, Water System Assets, Sarasota County, FL, 145.

CH2M HILL. (2007). "Fort Irwin water treatment process selection based on pilot testing results." *Water and wastewater utility systems capital improvement plan—Project W1*, Fort Irwin, CA.

Comstock, S. E., Boyer, T. H., and Graf, K. C. (2011). "Treatment of nanofiltration and reverse osmosis concentrates: Comparison of precipitative softening, coagulation, and anion exchange." *Water Res.*, 45(16), 4855–4865.

Fort Irwin Dept. of Public Works. (2011). "Fort Irwin year 2011 water quality report." ⟨http://www.irwin.army.mil/Community/Environment/Documents/Year2011WaterQualityReport.pdf⟩ (Jul. 19, 2012).

Gabelich, C. J., Rahardianto, A., Northrup, C. R., Yun, T. I., and Cohen, Y. (2011). "Process evaluation of intermediate chemical demineralization for water recovery enhancement in production-scale brackish water desalting." *Desalination*, 272(1–3), 36–45.

Gabelich, C. J., Williams, M. D., Rahardianto, A., Franklin, J. C., and Cohen, Y. (2007). "High-recovery reverse osmosis desalination using intermediate chemical demineralization." *J. Membr. Sci.*, 301(1–2), 131–141.

GE (General Electric). (2008). "GE reduces fluoride levels in potable water for the city of Suffolk using EDR technology." *Rep. CS1209EN*, Fairfield, CT.

GE (General Electric). (2009). "GE's EDR technology solves a unique set of water quality problems for Magna, UT." *Rep. CS1329EN*, Fairfield, CT.

Greenlee, L. F., Lawler, D. F., Freeman, B. D., Marrot, B., and Moulin, B. (2009). "Reverse osmosis desalination: Water sources, technology, and today's challenges." *Water Res.*, 43(9), 2317–2348.

GSA (Government Services Administration). (2012). "Design and construction services for a new electro-dialysis reversal (EDR) water treatment facility and water supply and distribution system infrastructure upgrades at Ft. Irwin, California." ⟨https://www.fbo.gov/index?s=opportunity&mode=form&id=c92d6cfaddd83a4f2af8105997bbed7e&tab=core&_cview=1⟩ (Jul. 16, 2012).

Hamilton Engineering. (2009). *Evaluation of lime softening versus electro-coagulation for treatment of produced water*, Denver.

Hammer, M. J. (1986). *Water and wastewater technology*, 2nd Ed., Wiley, New York.

Harries, R. C., Elyanow, D., Heshka, D. N., and Fischer, K. L. (1991). "Desalination of brackish groundwater for a prairie community using electrodialysis reversal." *Desalination*, 84(1–3), 109–121.

Jenicek, E. M., Carroll, R. A., Curvey, L. E., Hessel, M. S., Holmes, R. M., Pearson, E. (2011). "Water sustainability assessment for ten army installations." *Rep. U.S. Army Engineer Research and Development Center (ERDC)/Construction Engineering Research Laboratory (CERL) TR-11-5*, Vicksburg, MS.

Karahawa, T. (1994). "Construction and operation experience of a large-scale electrodialysis water desalination plant." *Desalination*, 96(1–3), 341–348.

Korngold, E., Aronov, L., and Daltrophe, N. (2009). "Electrodialysis of brine solutions discharged from an RO plant." *Desalination*, 242(1–3), 215–227.

Lee, L. Y., et al. (2009). "Integrated pretreatment with capacitive deionization for reverse osmosis reject recovery from water reclamation plant." *Water Res.*, 43(18), 4769–4777.

Lozier, J. C., Erdal, U. G., Lynch, A. F., and Schindler, S. (2006). *Evaluating traditional and innovative concentrate treatment and disposal methods for water recycling at Big Bear Valley, California*, CH2MHill, Tempe, AZ.

McHugh, J. M. (2014). "Army directive 2014-02 (net zero installations 609 policy)." Policy directive from the Secretary of the Army, Washington, DC.

Medina, V. F., Waisner, S. A., Johnson, J. L., Wade, R., Mattei-Sosa, J., and Brown, R. (2012). "Laboratory study for evaluating performance of unit processes to treat the electrodialysis reversal (EDR) reject stream for the proposed Fort Irwin water treatment plant." *U.S. Army Engineer Research and Development Center (ERDC) Rep. ERDC/EL TR-12-30*, Vicksburg, MS.

Mickley, M. (2008). *Survey of high-recovery and zero liquid discharge technologies for water utilities*, WateReuse Foundation, Alexandria, VA.

Mohammadesmaeili, F., Badr, M. K., Abbaszadegan, M., and Fox, P. (2010). "Byproduct recovery from reclaimed water reverse osmosis concentrate using lime and soda-ash treatment." *Water Environ. Res.*, 82(4), 342–350.

Ning, R. Y., Tarquin, A. J., and Balliew, J. E. (2010). "Seawater RO treatment of RO concentrate to extreme silica concentrations." *Desalin. Water Treat.*, 22(1–3), 286–291.

Ning, R. Y., Tarquin, A. J., Trzcinski, M., and Patwardhan, G. (2006). "Recovery optimization of RO concentrate from desert wells." *Desalination*, 201(1–3), 315–322.

Reynolds, T. D. (1977). *Unit operations and processes in environmental engineering*, PWS-Kent Publishing, Kent, U.K.

Scholze, R. J. (2011). "Water reuse and wastewater recycling at U.S. Army installations." *ERDC/CERL TR-SR-11-7*, U.S. Army Engineer Research and Development Center, Champaign, IL.

Schroeder, E., Tchobanoglous, G., Leverenz, H. L., and Asano, T. (2012). "Direct potable reuse: Benefits for public water supplies, agriculture, the environment, and energy conservation." National Water Research Institute (NWRI).

Sheikholeslami, R., Koo, T., and Lee, Y. J. (2001). "Silica fouling and cleaning of reverse osmosis membranes." *Desalination*, 139(1–3), 83–95.

Strathmann, H. (2004). "Assessment of electrodialysis desalination process costs." *Proc., Int. Conf. on Desalination Costing*, 32–54.

U.S. EPA. (1993). "Determination of inorganic anions in drinking water by ion chromatography." *EPA 300.1*, ⟨http://water.epa.gov/scitech/drinkingwater/labcert/upload/met300.pdf⟩.

U.S. EPA. (1994). "Determination of metals and trace elements in water and wastes by inductively coupled plasme-atomic emission spectrometry." *EPA 200.7*, ⟨http://www.docs-archive.com/EPA-200.7-Metals.pdf⟩.

U.S. EPA. (1999). "Total dissolved solids (TDS)." *EPA 160.1*, ⟨http://www.epa.gov/region9/qa/pdfs/160_1dqi.pdf⟩.

Valero, F., Barcelo, A., and Arbos, R. (2011). "Electrodialysis technology: Theory and applications." *Desalination: Trends and technologies*, M. Schorr, ed., InTech Open, Shanghai, China.

Wade, R. (1988). "New Bedford Harbor superfund project, report 7." *Rep. TR-EL-88-15*, U.S. Army Engineer Research and Development Center, Vicksburg, MS.

WRA (Water Reuse Association). (2012). "Seawater desalination costs." ⟨http://www.watereuse.org/sites/default/files/u8/WateReuse_Desal_Cost_White_Paper.pdf⟩ (Dec. 8. 2014).